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A Fundamental Characterization of Pulp Bleaching Effluents Produced Under Various Low-AOX Process Conditions

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A FUNDAMENTAL CHARACTERIZATION OF PULP BLEACHING EFFLUENTS PRODUCED UNDER VARIOUS LOW-AOX PROCESS CONDITIONS

A Thesis Submitted by

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SUMMARY

Because of environmental concerns surrounding the occurrence of certain chlorinated organic compounds in pulp bleaching effluents, the pulp and paper industry has substantially decreased the discharged level of total chlorinated organic material (measured as AOX, or adsorbable organic halide). Many different methods exist for decreasing AOX discharge, including "ECF" or "elemental chlorine-free" processes that utilize chlorine dioxide. It remains uncertain how much of an environmental benefit these processes actually are, or under what process conditions the maximum environmental benefits are achieved.

The objective of this thesis research was to determine, in an environmentally relevant and comprehensive manner, the chemical composition of the organic material in pulp bleaching effluents produced by low-AOX bleaching. Such a characterization may provide an increased understanding of the extent to which effluents formed in different bleaching processes cause adverse environmental effects and may indicate which low-AOX process conditions minimize the potential for adverse environmental effects.

An effluent characterization method based on ether extraction was developed and applied to effluents that were produced primarily under ECF bleaching conditions. Since the ether extract contains virtually all compounds known to be significant from an environmental perspective, the fractionation was based on ether extraction. It consisted of continuous ether extraction of bleaching effluents, fractionation of the ether extract into acidic, phenolic, and neutral subfractions, and determination of the ratio of chlorine atoms to carbon atoms for all effluents and effluent fractions. The ratio of chlorine to carbon atoms was determined for all effluent fractions because it is a predictor of environmental characteristics such as toxicity and lipophilicity.

In addition, the molecular weight distributions of bleaching effluents were determined, using a gel permeation chromatography method that was developed during this research. The proportion of low (< 1000) molecular weight material was determined. This proportion is significant from an environmental perspective, since the amount of low molecular weight material in an effluent may be related to the extent to which adverse environmental effects are caused by the effluent.

The results of this research provide additional evidence that ECF bleaching technologies are highly effective at decreasing the potential environmental threat of pulp bleaching. Both the use of 100% chlorine dioxide to replace chlorine, and the use of oxygen delignification prior to 100% chlorine dioxide bleaching, are likely to provide even greater environmental benefits than suggested by the AOX decreases associated with the processes. This is primarily due to a decreased proportion of material within environmentally significant fractions such as the ether soluble and phenolic fractions and a simultaneous decrease in the ratio of chlorine to carbon in these fractions. Decreased D stage reaction time and increased initial D stage pH, are likely to provide additional environmental benefits while maintaining effective delignification.

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INTRODUCTION

The presence of chlorinated organic compounds in the environment has become a serious issue to environmentalists and the public in general. Concern over certain toxic, carcinogenic, persistent, and bioaccumulating compounds such as chlorinated dioxins, polychlorinated biphenyls (PCB's) and pesticides, is warranted. However, a wide variety of chlorinated compounds, with an equally wide variety of properties exists. In fact, the majority of chlorinated organic compounds are innocuous and biodegradable, and some are even beneficial as drugs and food additives.[1]

Both the formation and destruction of chlorinated organic materials are naturally occurring processes.[1] Chlorinated organics are also generated by industry, and the process of pulp bleaching with chlorine-containing oxidants produces large quantities of chlorinated organics. However, process changes can essentially eliminate harmful compounds such as chlorinated dioxins, polychlorinated phenolic compounds, and chloroform.

Public concern over chlorinated organics and pressure by environmental groups have created market demand for "environmentally friendly" products, manufactured by processes that discharge low levels of chlorinated organics (measured by the adsorbable organic halide or AOX method). In addition to market demand, regulation of AOX is already implemented in several European countries and Canadian provinces,[2, 3] and is very likely to be implemented in the United States. Conventional chlorine bleaching of pulp produces about 5 kg AOX per air dry metric ton of pulp, and the regulations have limited, or eventually will limit AOX to less than 1.0 kg/ton.[2, 3] Regulation in the United States may limit AOX to less than 0.2 kg/ton.[4]

Many process options currently exist for reduction in the levels of AOX, and extensive research has been done in the areas of AOX discharge reduction, characterization

of effluents and effluent components, and environmental testing of effluents and effluent components. It remains uncertain what the effects of decreased AOX discharge will be on the environment, since reduction in the level of AOX does not necessarily mean the environmental impact of the effluent is decreased.[5-10] For example, effluents with similar levels of AOX can range from highly toxic to completely non-toxic.

The objective of this thesis research was to determine, in an environmentally relevant and comprehensive manner, the chemical composition of the organic material in pulp bleaching effluents produced by low-AOX bleaching. Such a characterization may provide an increased understanding of the extent to which effluents formed in different bleaching processes cause adverse environmental effects and may indicate which low-AOX process conditions minimize the potential for adverse environmental effects.

The thesis is organized as follows: It begins with a background section that reviews primarily bleaching process modifications for decreasing the discharge of AOX, bleaching effluent composition, and the environmental characteristics of bleaching effluents. Next, the thesis objective is outlined. The experimental approach section then explains how the proposed experiments will meet the thesis objective. The main body of the thesis, the results and discussion, is next and consists of 8 sections: a section explaining the organization, and 7 sections of actual results. A summary and conclusions section, recommendations for future work, a methods section, literature cited, and a series of appendices conclude the thesis.

BACKGROUND

The purpose of this review is to familiarize the reader with the general topic of chlorinated organic compounds in bleaching effluents. In particular, methods that decrease AOX discharge and effluent characteristics of both a chemical and environmental nature, are considered.

MEASUREMENT OF CHLORINATED ORGANIC MATERIAL

Both the AOX and TOCl (total organic chlorine) methods measure the total level of chlorinated organic material in bleach plant effluents. The AOX method is easier to perform and is less time consuming, has better reproducibility, a lower detection limit, and a higher percentage recovery of organic chlorine than the TOCl method.[11, 12] Therefore, it is the most widely used method for the measurement of total chlorinated organic compounds, and is the method upon which regulation is likely to be based.

Measurement of AOX[12-17] consists of adsorption of organic material onto activated carbon, separation of chloride ions from the chlorinated organics by displacement with nitrate ions, combustion of the activated carbon and organic chlorine to form HCl, and microcoulometric titration to determine the amount of chlorine. Adsorption can be done by passing the sample through columns packed with activated carbon,[12-15] or by adding activated carbon to the sample flask and shaking it.[12-14, 16, 17]

METHODS FOR DECREASING AOX DISCHARGE

During the bleaching of chemical pulps, residual lignin is removed and the pulp is brightened. The theory and practical aspects of pulp bleaching have been reviewed in de-

tail.[18, 19] The most commonly used bleaching sequences consist of several delignification stages, followed by brightening stages. The stages most often considered when comparing bleaching sequences with regard to effluent characteristics are the delignification stages, since 70-95% of the total pollution load is generated in them.[20] Only the delignification stages are considered here.

Delignification is often accomplished by treating the pulp with oxidants under acidic conditions to fragment lignin, followed by alkaline extraction to solublize the fragmented lignin. The most commonly used oxidants in the acidic delignification stages are chlorine[21] and chlorine dioxide.[22] The chlorine/chlorine dioxide stage will be referred to as the (CD) stage throughout this review, regardless of the relative amounts of Cl_2 and ClO_2 used or the oxidant addition sequence.

Oxygen and hydrogen peroxide are other oxidants commonly used to delignify pulp under alkaline conditions. Oxygen is used both in alkaline delignification stages preceding chlorine or chlorine dioxide delignification,[23] and after the (CD) stage as an oxidative enhancement in the first caustic extraction stage.[24, 25] Hydrogen peroxide is also used in oxidative extraction stages.

AOX is generated by substitution of chlorine atoms onto organic substrates (primarily lignin degradation products) present in the pulp, in carryover, or in the bleaching effluents. The total amount of AOX discharged into the receiving waters by a pulp mill can be decreased before or at the bleach plant by making process modifications, or after the bleach plant. Steps can be taken to reduce AOX levels before or at the bleach plant by decreasing the amount of lignin that reaches the (CD) stage. At the bleach plant, decreasing the amount of chlorine-containing oxidants contacting the pulp and its residual lignin also decreases the levels of AOX. Finally, post-mill treatment of bleaching effluents decreases the levels of AOX. These methods may be used alone, or in various com-

binations for greater AOX reduction. In the following section, several well established methods for decreasing AOX discharge are examined in greater detail.

Decreased Atomic Chlorine Charge

The quantity of chlorine-containing chemicals in the (CD) stage can be expressed a number of ways. Atomic chlorine charge refers to the total quantity of chlorine atoms present in all oxidants in the system. The molecular chlorine charge refers to only molecular chlorine (Cl_2 in equilibrium with HOCl) present in the system.

The active chlorine charge (also called equivalent chlorine) refers to the oxidizing power of chlorine and chlorine dioxide in the system, and is expressed in terms of chlorine equivalents. Chlorine dioxide contains 2.63 times more oxidizing equivalents per unit weight than chlorine.[19] A mole of ClO_2 can transfer 5 moles of electrons while a mole of Cl_2 can transfer only 2 moles of electrons. Therefore, 35.5 g of Cl_2 are required per mole of electrons transferred while 13.5 g of ClO_2 are required to transfer a mole of electrons, and on a weight basis ClO_2 contains (35.5/13.5) or 2.63 times more electrons for lignin oxidation than Cl_2.

All expressions of the oxidant charge are typically given as a weight percentage applied to the pulp. The charge expressed in this manner, divided by the kappa number of the pulp, is referred to as a multiple. For example, the active chlorine charge divided by the kappa number gives the active chlorine multiple. This is also referred to as the kappa factor.

Both delignification and AOX formation consume part of the chlorine or chlorine dioxide charge. The amount of AOX formed during bleaching is nearly proportional to the charge of atomic chlorine, in both the Cl_2 and ClO_2, within the (CD) stage,[8, 26-32] as

shown in Figure 1. The same proportion of the atomic chlorine charge (about 8-10%)[6] becomes bleach plant AOX whether it originates from Cl_2 or ClO_2.[26]

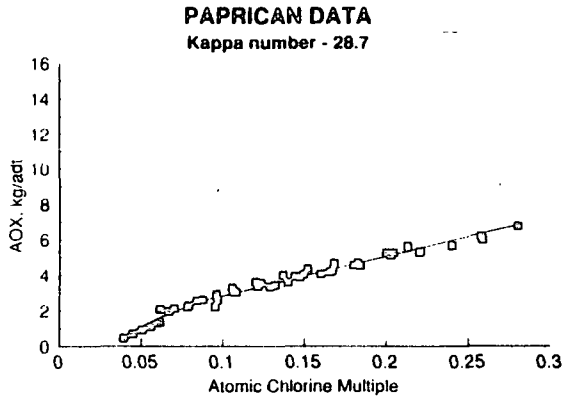

Figure 1. AOX Formation at Various Oxidant Charges. (Reproduced from reference 8, by permission of the Canadian Pulp and Paper Association)

Chlorine Dioxide Substitution

The atomic chlorine charge can be decreased by partially or completely replacing Cl_2 with ClO_2 in the (CD) stage. Higher ClO_2 substitution decreases the atomic chlorine charge at the same total oxidant level, since chlorine dioxide has more oxidizing power per unit of atomic chlorine. The decreased atomic chlorine charge produces less AOX.

Low levels of ClO_2 addition in the (CD) stage (< 15%) have traditionally been implemented to protect pulp viscosity,[19, 20] but environmental concerns surrounding Cl_2 have recently led to substantially greater use of ClO_2 (50% or more substitution). Conversion of a (CD) stage from low to high ClO_2 substitution is relatively simple and inexpensive, with only additional pipes, pumps, mixers, and flowmeters required.[33] Chlorine and chlorine dioxide can be added several different ways: sequentially with Cl_2 first, se-

quentially with ClO_2 first, or combined. The addition of ClO_2 first generally gives better bleaching efficiency.[34, 35] Maximum delignification occurs at about 50% ClO_2 substitution,[34] and 50% ClO_2 delignifies more efficiently than 100% ClO_2.[36]

Increased ClO_2 substitution decreases AOX levels between 10 and 90% as shown in Table I. Results are dependent on the wood species, the pulping process, the extent of ClO_2 substitution, and on other operating conditions. At constant chemical charges, sequential addition of the oxidants with Cl_2 first, or combined addition of Cl_2 and ClO_2, both produce lower levels of AOX than sequential addition with ClO_2 first.[37, 44] However, when bleaching to a constant final kappa number, lower levels of AOX are produced when chlorine dioxide is added first, since this mode of addition more effectively delignifies and requires a smaller oxidant charge per unit of lignin.[35]

Oxidative Extraction

Caustic extraction stages may be reinforced with oxidants such as oxygen, hydrogen peroxide, or a mixture of the two. The extraction stages are then referred to as (EO), (EP), or (EOP) stages respectively. Oxidants in the extraction stage remove additional lignin after the (CD) stage. This either decreases the pulp kappa number after the extraction stage, or decreases the oxidant charge per unit of lignin required in the (CD) stage to maintain a constant kappa number.

If the objective is to maintain a constant kappa, less lignin must be removed in the (CD) stage, and a lower active chlorine charge is applied. When a process change decreases the active chlorine charge requirement, the size of the Cl_2 portion of the charge alone can be decreased, and while the absolute amount of ClO_2 remains constant, the percent substitution increases. Therefore, the required active chlorine charge is decreased

but the atomic chlorine charge is decreased more because of the increased ClO_2 substitution, and the AOX level is proportionately decreased.

Table I. Decreased AOX Formation by ClO_2 Substitution.

Low Substitution		High Substitution			
% ClO_2	AOX (kg/t)	% ClO_2	AOX (kg/t)	AOX Red. (%)	Reference
17	3.8	50	3.0	21	31
10	3.5	48	2.4	31	33
48	2.4	58	1.0	58	33
10	4.8	50	3.4	29	37
10	4.8	90	2.2	54	37
15	2.9	100	0.2	93	38
0	5.3	50	3.0	43	39
15	----	75	----	45	40
0	6.7	10	5.9	12	41
0	6.7	90	2.2	67	41
0	6.7	100	1.7	75	41
75	0.55	100	0.47	15	42
30	2.0	50	1.5	25	43
50	1.5	100	0.9	40	43

A very common use of oxygen in pulp bleaching is in the (EO) stage, because of its simplicity and low investment cost. Only minor modifications are needed to convert a conventional caustic extraction stage to an (EO) stage. The critical operation is the mixing of oxygen with a medium consistency pulp suspension and retention of the gas long enough (3-5 minutes) for reaction.[45, 46] A normal upflow extraction tower can be con-

verted to an (EO) stage by adding a medium consistency mixer for oxygen addition, and a downflow extraction tower can be converted to an upflow-downflow (EO) stage by adding a pre-retention tube between the mixer and the downflow tower. Because of more effective extraction, an (EO) stage decreases the post-extraction kappa number by 25% compared to a conventional E stage.[47]

Hydrogen peroxide can also be added to an E stage to enhance lignin removal. An existing (EO) stage is relatively easy to convert to an (EOP) stage. Hydrogen peroxide, as a 5-10% aqueous solution, is simply added before the oxygen mixer. This mode of addition ensures that oxygen and peroxide, which react more efficiently together, are present in the sequence together.[48] An (EOP) stage can reduce the post-extraction kappa number by 40-45%,[47] or can allow a 20-30% reduction of the active chlorine charge[48] compared to a conventional caustic extraction.

Table II shows the AOX reductions (between 20 and 50%) caused by oxidative extraction stages. In each case, additional delignification done after the (CD) stage by extraction stage oxidants allowed a decreased (CD) stage oxidant charge, while maintaining pulp brightness.

High Temperature Oxidative Extraction. The high temperature (EO) stage is another variation of oxidative extraction in which the temperature of the stage is increased from the standard 60°C, to 90°C or greater, and oxygen pressure is increased. The increased temperature and pressure allow additional delignification compared to a normal (EO) stage.[51, 52] A further decrease in the charge of chlorine-containing oxidants occurs, and the AOX decreases correspondingly. The reduction in applied active chlorine multiple or the increased ClO_2 substitution allowed by the hot (EO) stage, decreases AOX levels by 30-45%.[51]

Table II. Decreased AOX Formation by Oxidative Extraction.

Conventional		Oxidative			
Stage	AOX (kg/t)	Stage	AOX (kg/t)	AOX Red. (%)	Reference
E	----	(EOP)	----	35	40
E	5.6	(EOP)	3.2	43	47
E	6.8	(EOP)	4.0	41	47
E	6.4	(EO)	4.9	23	49
E	3.9	(EO)	1.9	51	49
(EO)	4.2	(EOP)	3.1	26	50

Decreased Lignin Content

The amount of AOX generated within a bleach plant is dependent on the effective lignin content of the pulp entering the (CD) stage. Residual lignin within the pulp and dissolved lignin in carryover both contribute to the effective lignin content of the pulp, and are both substituted by chlorine atoms in the (CD) stage, and both form AOX. A decrease in the quantity of either residual lignin or dissolved carryover lignin entering the (CD) stage in the bleach plant, decreases the quantity of AOX.[8, 28, 34, 41, 53-57] The decrease in AOX levels with decreasing kappa number before the (CD) stage, is in some cases linear[8, 55, 56] as shown in Figure 2.

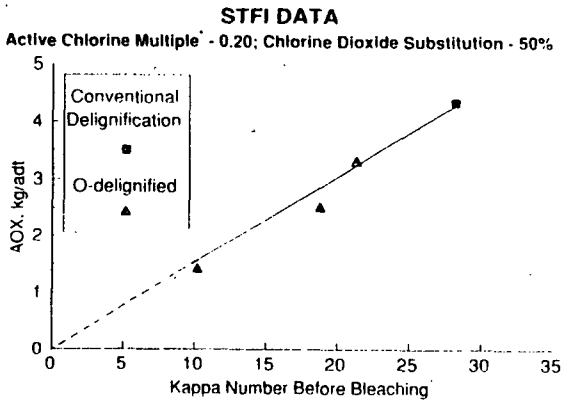

Figure 2. AOX Formation for Different Pulp Kappa Numbers. (Reproduced from reference 8, by permission of the Canadian Pulp and Paper Association)

Improved Pulp Washing

One way to remove additional lignin and decrease AOX formation, is to improve the brownstock washing at the pulp mill. An average level of carryover for unbleached softwood is about 5 kappa units, and for oxygen bleached softwood an average level of carryover is about 3 kappa units.[53] Carryover can vary between 0.5 and 9.8 kappa units, depending on pulp type and the level of washing.[58] Washing efficiency may be improved by preventing washer overloading, and by supplying additional shower water.[59]

Improved pulp washing can decrease the levels of AOX by about 20%.[60] About 10-20% of the total AOX can be attributed to carryover in well washed pulps, while 25-40% of the total AOX can be due to carryover if washing is not well controlled.[58] Black liquor carryover to the (CD) stage forms the same level of AOX as residual lignin,[53, 61] while oxygen stage carryover to the (CD) stage forms more AOX per unit of carryover than either black liquor carryover or residual lignin.[53, 58, 61] Good pulp washing may therefore be more important when oxygen bleaching is used.

Extended Delignification

Increased delignification in pulping is achieved by more selective cooking processes, which remove more lignin while maintaining pulp strength. Additional removed lignin is routed to the recovery system, producing energy and reducing the effluent organic load.

The selectivity of pulping is improved in modified kraft cooking by maintaining a smooth alkali charge profile throughout the cook, by maintaining high sulfidity, and by decreasing the dissolved lignin content in the liquor near the end of the cook.[55, 62, 63] Modified batch cooking and modified continuous cooking both achieve improved selectivity.

In the modified batch process, the lignin concentration near the end of the cook is decreased and the alkali profile is made smoother by displacement of the spent liquor with fresh wash liquor of sufficiently high sulfidity to maintain delignification.[63] The kappa number of pulps produced by modified batch systems can be decreased from a conventional level of greater than 30, to 25 or less without loss of pulp viscosity.[56, 60, 63] Another form of modified batch cooking, the RDH process, can achieve 16 kappa pulps without viscosity loss.[42]

Modified continuous cooking is accomplished through the modification of a two vessel Kamyr continuous digester to allow the introduction of white liquor at several locations and countercurrent liquor flow during the final cooking phase.[62] Pulps with kappa numbers 5-6 units less than conventional pulping can be produced by this system[43, 62] and oxygen bleached pulps with kappa numbers as low as 12 can be produced.[43]

Examples of AOX reduction achieved by extended delignification, are given in Table III, and range from 10 to 70%. Because of the lower kappa numbers of pulps pro-

duced by extended delignification, less lignin must be removed by chlorine-containing bleaching chemicals, and less AOX is produced when these pulps are bleached.

Table III. Decreased AOX Formation by Extended Delignification.

Conventional		Extended			
Kappa	AOX (kg/t)	Kappa	AOX (kg/t)	AOX Red. (%)	Reference
33	3.1	16	1.4	55	42
17	1.7	8.5	0.6	65	42
24	2.7	11	0.9	67	42
18	2.3	13	2.0	13	43
27	3.7	21	2.4	35	55
32	1.9	25	1.5	21	64
32	5.5	25	4.5	18	65
18	3.5	14	2.5	29	65

Oxygen Delignification

Oxygen can be applied to pulp in several ways. It can be used for delignification before the (CD) stage in a high consistency or medium consistency pressurized tower, or in a lower pressure oxidative pre-extraction stage. It can also be used as an oxidative addition to the caustic extraction stage, as previously discussed.

Oxygen delignification removes lignin more selectively than the final part of the kraft cook, which makes it possible to delignify the pulp to a greater extent before the (CD) stage without serious strength loss.[23, 66] Pulps with kappa numbers as low as 16

can be produced by oxygen bleaching of conventionally cooked kraft pulps.[56] The material removed by oxygen bleaching is routed to the recovery system and burned, reducing the bleach plant effluent load and producing energy.

Most early oxygen delignification systems were high consistency (HC) systems, operating at 25-30% consistency and 100-125°C. In such systems, a press is required to increase pulp consistency before the addition of chemicals. HC oxygen bleaching systems typically achieve 45-50% delignification.[66]

Medium Consistency (MC) oxygen bleaching has become the preferred method of oxygen bleaching since the rather recent development of the medium consistency gas mixer. The process requires a smaller capital investment than the HC system, since bleaching is done at 10-14% consistency and a press is not required. MC systems typically achieve 40-45% delignification,[66] but higher levels of delignification are possible.[42]

Oxygen bleaching leads to AOX reductions between 30 and 70%, as shown in Table IV. Because of the lower kappa number of oxygen bleached pulps before the (CD) stage, less lignin must be removed by chlorine-containing chemicals, and less AOX is formed when these pulps are bleached.

Oxidative Pre-Extraction. Existing bleach towers can be converted to low pressure oxygen stages with only a small capital investment.[45] Only an upflow pre-retention tube must be added to an existing downflow tower to allow sufficient oxygen contact with the pulp for significant delignification. Such (EO) or (EOP) pre-extractions can achieve up to 30% delignification, or kappa reductions of up to 10 units.[41, 45, 68] Softwood pulps with kappa numbers near 20 are possible using oxidative pre-extraction.[41, 45]

Table IV. Decreased AOX Formation by Oxygen Bleaching.

Unbleached		Oxygen Bleached			
Kappa	AOX (kg/t)	Kappa	AOX (kg/t)	AOX Red. (%)	Reference
30	5.9	17	3.9	34	41
30	4.7	17	2.4	49	41
30	1.7	17	0.3	82	41
28	3.0	15	1.4	53	41
33	3.1	17	1.7	45	42
38	10.0	17	3.2	68	53
32	5.5	18	3.5	36	65
25	4.5	14	2.5	44	65
32	5.4	20	3.4	37	67

The additional delignification before the (CD) stage results in decreased AOX levels. An (EO) pre-extraction can decrease AOX levels up to 40%, while with the addition of hydrogen peroxide AOX reductions of 70% are possible.[41]

Post-Mill Treatment of Effluents

Once formed in the mill, AOX can still be eliminated from the effluent before discharge to the environment, by effluent treatment. Treatment methods include both conventional secondary biological treatment and alternative methods.

Conventional secondary biological treatment systems include aerated stabilization basins[6, 33, 65, 68-72] and activated sludge treatment[6, 73] which remove between 20 and 75% of the total AOX. Typical removal is about 40 to 50%. The AOX in effluents produced using 100% chlorine dioxide bleaching may be more degradable by conventional treatment than that produced by lower levels of substitution.[70]

Other biological systems also remove AOX. Application of an anaerobic treatment step,[74] or aerobic and anaerobic biofilm treatment[75, 76] may increase AOX removal. The term biofilm refers to a supported biological phase rather than a suspension of biological material. A biofilm reactor can decrease the level of AOX in secondary treated effluent by 30-42%[76] and could therefore represent an advantage over other treatment steps, since it is able to degrade material that is not degraded by conventional secondary treatment. White rot fungus can decrease effluent AOX by about 50%.[70]

Non-biological methods for AOX destruction also exist. Although in most effluent treatment systems alkaline and acid effluents are mixed, increasing the pH of the (CD) stage effluent, additional pH adjustment may be beneficial for AOX reduction. Effluents from the (CD) stage of bleaching are quite unstable to elevated pH levels, and their AOX levels can be decreased up to 75% by adjusting the pH to about 12.[77-79] The level of AOX in combined stage effluents can be similarly decreased by increasing their pH.[80, 81] Addition of weak black liquor, Na_2CO_3, or Na_2S to bleaching effluents can all decrease AOX levels in effluents.[78, 81] Treatment of (CD) stage effluent with UV irradiation at low pH, or particularly in addition to alkali treatment, can decrease AOX levels by over 90%,[77] and direct sunlight can decrease AOX levels by over 30% in both treated and untreated mill effluents.[82]

Other methods remove AOX from the effluent stream without destroying it, and the AOX must be subsequently burned or disposed of as sludge. Such methods include

adsorption of AOX by boiler ash carbon,[69] adsorption by activated carbon,[83] and ultrafiltration of effluents.[84]

EFFLUENT CHARACTERISTICS

Chemical characterizations include the identification and quantification of effluent components, and the determination of chemical properties of effluents or the components of effluents. Environmental characterizations directly measure the impact of an effluent or effluent component on the environment but do not necessarily consider effluent composition.

Chemical Characterizations

Chemical characterization methods considered here include the identification and quantification of components of bleaching effluents, measurement of bleaching effluent component lipophilicity, determination of effluent molecular weight distributions, and the determination of chlorine to carbon ratios of effluents.

Isolation and Quantification of Individual Compounds

Volatile compounds, carbohydrates, phenolics, carboxylic acids, and various types of neutral compounds have all been identified in bleaching effluents. Several extensive lists of identified compounds exist.[85, 86] Reference 86 identifies over 300 compounds in bleaching effluents, gives the quantities present, and depicts the chemical structure of each.

Identification and quantification of individual compounds occurs because of special interest in them. For example, highly toxic, bioaccumulating, mutagenic, or persistent compounds are often examined individually because of the potential problems they may cause. Specific compounds that have been considered extensively in bleaching literature are chlorinated phenolics, chloroform, and chlorinated dioxins.

Volatile Compounds. Among the potentially volatile compounds commonly found in bleaching effluents are methanol, carbon dioxide, formic acid, and acetic acid,[87-89] and chloroform. Among these chloroform is of greatest interest because it is considered a hazardous air pollutant.

Chloroform. Chloroform leaves the mill through vents and in bleach plant effluents. Much of the chloroform released in effluents is volatilized during waste treatment and becomes an air pollutant.

The majority of chloroform generation occurs in the hypochlorite stages of bleaching,[90-93] and the elimination of hypochlorite stages reduces chloroform vent emissions by over 70%.[94] The hypochlorite stage is a now outdated alkaline, sodium hypochlorite-based stage, that was once widely used to achieve high brightness.

In mills that do not use hypochlorite, most of the chloroform generation occurs in the (CD) stage.[92] Decreased (CD) stage atomic chlorine consumption,[27, 91, 92] decreased kappa number pulp entering the (CD) stage,[29] increased chlorine dioxide substitution for chlorine[27, 38, 39, 91, 92] and addition of Cl_2 before ClO_2 in a sequential addition[92] all reduce chloroform emissions. Lower (CD) stage temperature,[90, 91] high caustic extraction stage pH,[92] efficient (CD) stage mixing,[39] and higher (CD) stage consistency[39] also re-

duce chloroform emissions. More chloroform is produced in the bleaching of softwood than in the bleaching of hardwood.[90-92]

Carbohydrates. Another identified component in bleaching effluents is carbohydrate fragments. The high (> 1000) molecular weight portion of the effluent is rich in carbohydrate fragments,[87-89, 95] and caustic extraction stage effluents contain more carbohydrate components than (CD) stage effluents.[87, 89] Monosaccharide analysis of the component sugars indicates that the carbohydrate material consists of units commonly found in hemicellulose, including arabinose, galactose, glucose, mannose, and xylose.[87-89, 95]

Carboxylic Acids. Carboxylic acids of many different structural types have been identified in bleaching effluents, and include monobasic acids, dibasic acids, aromatic acids, resin acids, and fatty acids. Identified monocarboxylic acids include choroacetic acids,[31, 34, 96] and lactic, glycolic, glyceric, and chloropropenoic acids.[88, 89, 97] Dicarboxylic acids include oxalic, malonic, succinic acids and the chlorinated analogs of some of these acids.[88, 89, 97] Aromatic acids include benzoic acid, benzene dicarboxylic acid, and chlorinated hydroxy and methoxy substituted benzoic acids.[97] Furancarboxylic and thiophenecarboxylic acids are other identified carboxylic acids that include 5-membered ring structures.[97] Examples of resin acids present in bleaching effluents are pimaric, isopimaric, abietic, and dehydroabietic acids; examples of fatty acids are oleic, linoleic, and 9,10-epoxystearic acids.[98]

Increased ClO_2 substitution for Cl_2,[34, 96] and decreased consumption of atomic chlorine[31] decrease the levels of chlorinated acetic acids. However, effluents from chlorine-based bleaching of oxygen bleached pulp contain more chlorinated acetic acids than effluents from bleaching of unbleached pulp.[34, 96]

Phenolics. A variety of different chlorophenolic compounds, including chlorinated phenols, guaiacols and catechols, are commonly found in bleach plant effluents.[99-105] Chlorovanillins have also been detected in effluents,[99, 100, 102, 103] and syringaldehydes and syringols are found in hardwood bleach plant effluents.[100, 102] Chlorophenolics are of interest because some are known to be toxic.

The effect of bleaching variables on the formation of individual chlorinated phenolic compounds has been studied extensively. Dichlorophenolics and trichlorophenolics generally reach maximum concentrations at molecular chlorine multiples of 0.1 and 0.2 respectively, while tetrachlorophenolic compounds reach maximum concentrations at multiples greater than 0.25.[8, 26, 27, 67] A decreased pulp kappa number before the (CD) stage decreases the levels of individual chlorophenolics.[8, 26, 29, 34, 54, 67, 96] When moderate increases in ClO_2 substitution are made, fewer tri- and tetrachlorinated phenolics and more mono- and dichlorinated phenolics are formed.[31, 37, 39, 58, 67, 96]

The effect of bleaching variables on total chlorinated phenolic formation (sum of all determined chlorinated phenolics) has also been studied extensively. The total quantity of chlorinated phenolics reaches a maximum as the chlorine charge increases, and then decreases at higher charges.[32, 99, 100, 102] The total chlorophenolic content decreases as the unbleached pulp kappa number decreases,[20, 34, 41, 43, 53, 67, 96, 106] for example through the implementation of oxygen bleaching or extended delignification. The total chlorophenolic content of effluents reaches a maximum at about 50% ClO_2 substitution and decreases beyond this.[20, 34, 37, 41, 100, 102] However, in many cases the total level of chlorinated phenolics has decreased as ClO_2 substitution was increased.[38, 39, 43, 96, 99, 103, 106] At 100% ClO_2 substitution, the level of all chlorinated phenolics is substantially decreased compared to lower substitution levels.[38, 41, 43, 96, 99, 103]

Higher final (CD) stage pH,[99, 100, 102] lower (CD) stage temperature,[99, 102] increased (CD) stage consistency,[39] improved (CD) stage mixing,[39] minimization of carry-

over by improved pulp washing, [58] and the addition of Cl_2 before ClO_2 in a sequential addition,[35, 37] all lead to the production of fewer phenolics. The total level of chlorinated phenolics present in hardwood effluents is typically lower than that in softwood effluents.[99, 100]

Neutral Compounds. Neutral compounds of many structural types have been identified in bleaching effluents, and they are of interest because of their mutagenic behavior. Identified neutral compounds in (CD) stage effluents include 2-chloropropenal,[107-109] 2, 3-dichloropropanal,[109] chloroacetones,[6, 58, 107-110] 3-chloro-4-dichloromethyl-5-hydroxy-2(5H)-furanone (or MX),[110, 111] chlorinated methylene furanones,[112] chlorinated pyrones,[112, 113] chlorinated thiophenes,[93, 105, 110, 113] and chlorinated dimethyl sulfones.[29, 38, 96, 108, 110]

The level of chlorinated acetones in effluents decreases with a decreased chlorine multiple and with increased ClO_2 substitution for chlorine.[58] However, chlorinated acetone levels are not affected by the level of carryover to the bleach plant.[58] On the other hand, chlorinated thiophene precursors are formed in the pulping process and their levels in bleaching effluents can be decreased by improved pulp washing.[93]

Dichlorodimethyl Sulfone. A sulfur containing chlorinated neutral compound that deserves consideration is 1,1-dichlorodimethyl sulfone (DDS), since it is present in relatively high quantities in bleaching effluents and is very persistent, remaining essentially unchanged through effluent treatment.[110] The level of DDS decreases as the kappa number before the (CD) stage decreases, for example by oxygen bleaching[29] and as ClO_2 substitution for chlorine increases.[38, 96] However, oxygen bleaching before 100% ClO_2

substitution increases levels of DDS.[96] Since dimethylsulfones originate in the kraft pulping process, improved pulp washing can reduce their levels in effluents.

Chlorinated Dioxins. Although chlorinated dioxins and furans (2,3,7,8-TCDD and TCDF) are present in very small quantities in bleach plant effluent, there is still concern about them because of toxicity and persistence. A considerable amount of research has been done in the areas of dioxin analysis and the reduction of dioxin levels through bleaching process changes.

The formation of chlorinated dioxins can be decreased to non-detectable levels by some of the same methods that have been used to decrease the levels of total AOX and chlorinated phenolics. A decreased atomic chlorine charge[26, 27, 50, 114, 115] and increased ClO_2 substitution for chlorine[27, 35, 50, 114] both reduce the levels of dioxins. Split addition of chlorine in the (CD) stage also reduces dioxin levels[116] due to a decreased effective charge of atomic chlorine at any given time. Below molecular chlorine multiples of about 0.15 dioxin formation is very low,[8, 26, 117] because unlike AOX formation 2,3,7,8-TCDD and 2,3,7,8-TCDF are not formed until a critical charge of chlorine is exceeded (Figure 3). Increased final (CD) stage pH,[114, 116] decreased (CD) stage consistency,[114] and addition of Cl_2 before ClO_2 in a sequential addition[35, 114] all produce smaller quantities of dioxins in bleaching effluents.

The formation of dioxin is not affected by the kappa number of the pulp before the (CD) stage.[8, 114, 117] This is shown in Figure 3, where dioxin formation levels from the bleaching of pulps with different kappa numbers fall on the same curve. This is explained by hypothesized mechanisms for dioxin formation, in which precursors originate prior to bleaching and are chlorinated in the (CD) stage of bleaching.[59, 115, 117] Dioxin precursors have been identified in unbleached brownstock samples, and the formation of

chlorinated dioxins is decreased when pulp washing is improved and precursors are more effectively washed away.[59, 118]

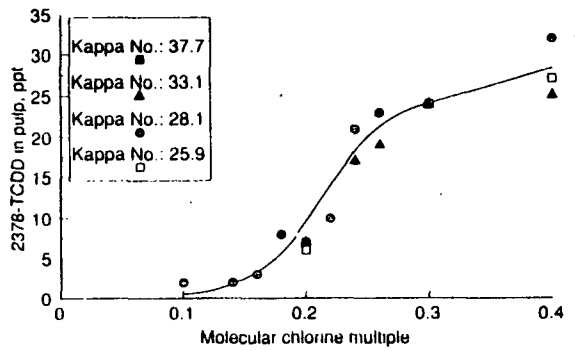

Figure 3. Dioxin Formation at Various Chlorine Charges. (Reproduced from reference 8, by permission of the Canadian Pulp and Paper Association)

One possible source of dioxin precursors is contaminated oil based defoamers. Addition of defoamers that are contaminated by dioxin precursors increases dioxin levels, while addition of defoamers that are free of precursors does not.[118] In fact, the formation of 2,3,7,8-TCDD and TCDF in bleaching are linearly related to the applied charge of precursor contaminated defoamer.[118]

Lipophilicity Determinations

The lipophilicity indicates how strongly a solute favors an organic substrate over the aqueous phase. The standard method for measuring the lipophilicity of organic material is the octanol/water partition coefficient (P_{ow} or K_{ow}). The K_{ow} is the ratio of the solute concentration extracted into octanol to the concentration in the water sample. The

purpose of the K_{ow} measurement is to predict biological accumulation; K_{ow} values correlate with bioconcentration[119] and with acute toxicity.[120] The K_{ow} values for components of bleaching effluents vary widely, from less than 1 for very polar, acidic solutes, to in excess of 100,000 for tetrachlorophenols, to several million for hexachlorobenzene.[85] Figure 4, which graphs some compiled data from reference 85, shows that the log K_{ow} increases with the number of chlorine atoms per molecule, for several classes of compounds.

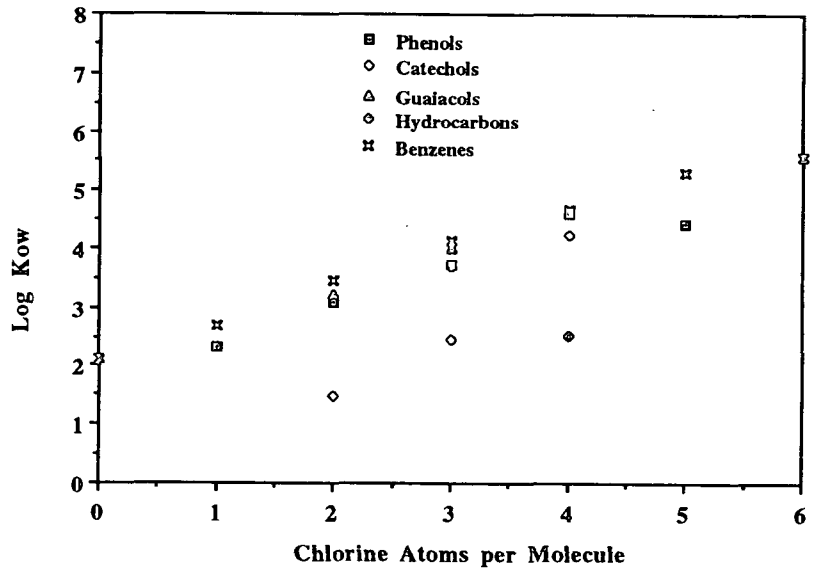

Figure 4. Lipophilicity of Bleaching Effluent Compounds. (Data from reference 85)

The K_{ow} of bleaching effluents cannot be readily determined because of problems, such as the formation of emulsions.[120] Therefore, alternate methods for estimating effluent lipophilicity are used.

Solvent Extractable Organic Halogen. One method for estimating effluent lipophilicity is solvent extractable organic chlorine. The EOX method employs solvents such as heptane, pentane, hexane, and cyclohexane to extract the most lipophilic portion of the effluent. Diethyl ether extraction is also used, and removes more material from the effluent than EOX methods.[31] In both cases AOX analysis is done on the solvent sample. Usually 1% or less of the AOX is contained in the EOX fraction,[10, 96, 122] while 5-10% of the AOX is extracted by ether.[72, 97]

Solvent extractable organic halide formation is linearly proportional to the atomic chlorine charge[31, 57] as is the case for AOX formation. Essentially no EOX is formed when the level of consumed atomic chlorine is below a critical value.[57] This is similar to what occurs during the formation of dioxins. EOX is also related linearly to AOX formation,[26, 27, 57] and there is a critical level of AOX below which very little EOX is detected.[26, 57] Therefore, EOX can be essentially zero while the AOX is measurable.

The effect of ClO_2 substitution on solvent extractable AOX is further illustrated in Table V, where solvent extractable AOX decreases between 40 and 90% when ClO_2 substitution for chlorine is increased. In fact, the ether extractable organic chlorine decreases linearly with increased ClO_2 substitution, for conventional, modified and oxygen bleached pulps.[34] In addition, the proportion of the AOX that is solvent extractable decreases as ClO_2 substitution is increased.

The amount of dissolved and residual lignin entering the (CD) stage, has an effect on the formation of solvent extractable AOX. A lower kappa number pulp entering the (CD) stage produces less solvent extractable AOX when bleached with chlorine-based chemicals.[34, 53, 54, 61, 96] Black liquor carryover contributes to the level of solvent extractable AOX in effluents from the subsequent bleaching stages,[53, 54, 61] and may produce more solvent extractable AOX per kappa unit than residual lignin.[53] Oxygen stage

carryover to the (CD) stage contributes more solvent extractable AOX per kappa unit, than either black liquor carryover or residual lignin.[53, 61]

Table V. Decreased Solvent Extractable AOX Formation by ClO_2 Substitution.

Low Substitution		High Substitution			
% ClO_2	Ext. AOX (g/t)	% ClO_2	Ext. AOX (g/t)	Reduction (%)	Reference
17	205	50	120	41	31
17	37	50	24	35	31
15	70	100	4	94	38
0	68	50	12	82	39
10	8	100	0.9	89	96

Chromatographic Methods. Reversed phase thin layer chromatography (RPTLC)[32, 67, 96, 105, 112, 123, 124] and reversed phase high performance liquid chromatography (RPHPLC)[121, 123] are chromatographic methods used to determine effluent lipophilicity. Unlike normal phase chromatography, reversed phase chromatography uses a non-polar stationary phase and a polar solvent. The partition coefficients derived from this type of system have good correlations to octanol/water coefficients.[121, 123, 124] Using reversed phase chromatography, the lipophilic fraction of the effluent (that with a large K_{ow}) can be isolated and examined. Compounds with a $K_{ow} > 1000$ represent less than 1% of the total AOX,[105, 122] and less than 20% of the already small EOX fraction.[122]

The size of the lipophilic fraction of bleaching effluents is decreased by using a decreased atomic chlorine multiple during bleaching,[67] by a reduced kappa number pulp entering the (CD) stage of bleaching,[29, 67, 96] and by increased ClO_2 substitution for chlorine.[29, 67, 96]

Molecular Weight Distributions

Molecular weight distributions are of interest, from an environmental point of view, because low (< 1000) molecular weight material is more easily degraded biologically[71, 72, 78, 125] but the quantity of low molecular weight material may correlate with environmental parameters such as acute toxicity.[5, 83, 125] High molecular weight material is less toxic[95, 126] and is not degraded as well by conventional effluent treatment. Molecular weight distributions of bleaching effluents have been determined by ultrafiltration[88, 89, 93, 127-131] and by gel permeation chromatography (GPC).[95, 131]

Ultrafiltration is pressurized filtration of solutions containing different molecular weight materials, using membranes with pores of known sizes. By using a series of such filters in succession, beginning with one that retains only large molecules and ending with one that only small molecules can pass through, a distribution of molecular weight may be achieved.

Gel permeation chromatography (GPC), also called size exclusion chromatography, is the elution of solutions which contain a mixture of different molecular weight materials, through columns packed with porous gels. The gels contain pores with a known distribution of sizes. Large molecules may enter only few of the pores, have less column volume available to them, and elute first. Smaller molecules may enter more pores, have a larger available column volume, and elute later.

The two methods give extremely different molecular weight distributions, with GPC results indicating much more low molecular weight material than ultrafiltration.[131] In the case of (CD) stage effluent, GPC shows about 80% of the total material with a molecular weight of less than 1000[95] while ultrafiltration shows 30% in this class.[93] Both methods indicate considerably more low (< 1000) molecular weight material within the (CD) stage effluents than in the E stage effluents.[87-89, 95, 128, 129] This is expected since alkali will swell and open the pore structure of pulp fibers, allowing larger lignin fragments to be removed.

The molecular weight distributions of effluents from different bleaching sequences have primarily been compared using ultrafiltration. Results are rather limited, and the effluents tested have not usually been produced under well controlled conditions. Effluents produced using high chlorine dioxide substitution in the (CD) stage have exhibited a greater proportion of low molecular weight material,[96, 129] or the same proportion[71] as effluents produced using mostly chlorine. The effect of oxygen bleaching on the molecular weight distribution is also somewhat uncertain, since studies have indicated that O_2 delignification produces a greater proportion of low molecular weight material[70] and a smaller proportion of low molecular weight material[88, 89] in the subsequent bleaching stages.

Separation effectiveness by ultrafiltration is uncertain and is highly dependent on the concentration of the effluents.[131] In some cases of ultrafiltration, low molecular weight material has been detected in the high molecular weight fraction.[108, 132] Fractionation by GPC is more successful, since few low mass compounds are present in the high molecular weight fraction.[95]

Chlorine To Carbon Ratio Determination

The ratio of chlorine atoms to carbon atoms of the organic material in bleaching effluents, or in fractions of effluents, may be important from an environmental point of view. Within certain classes of compounds found in bleaching effluents, environmental characteristics such as lipophilicity[105, 133] and toxicity[101, 102, 134] correlate with the ratio of chlorine to carbon of the material.

The ratios (expressed as chlorine atoms per 100 carbon atoms) vary widely, from less than 1 to greater than 10, depending on the type of bleaching and whether the effluents are from (CD) or E stages, or are combined mill effluents. The ratio of chlorine to carbon is much lower in E stage effluents than in those from the (CD) stage.[128, 129] Chlorine dioxide substitution for chlorine decreases the ratio substantially,[71, 96, 128, 129, 135] and oxygen bleaching may decrease the ratio in effluents from subsequent bleaching stages.[96]

Environmental Characterizations

Environmental characterization of effluents includes determinations of acute and chronic toxicity, mutagenicity, bioaccumulation, and environmental persistence. These tests directly show the effects of effluents or effluent components on the health of organisms in the environment. Such tests are biological in nature, and involve test organisms such as fish or bacteria. The tests are highly dependent on conditions and on the test species used, and the results of different studies are therefore often difficult to compare.

Accumulation of Effluent Components

Certain bleach plant effluent components accumulate in aquatic life because of their non-polar, lipophilic character. Methods exist for quantifying the accumulation of bleach plant effluent components. In these techniques, pollutants that have collected in the tissue of aquatic organisms are measured.

Bioaccumulation. In bioaccumulation studies, fish or other aquatic life taken from bleach plant receiving waters are analyzed for effluent components and compared with those taken from an effluent-free region of the same body of water.

The total organic material extracted from the fat of fish captured near a bleach plant effluent source is considerably higher than that of reference fish collected away from the effluent source.[136, 137] When effluent discharge stopped, the extractable organic chlorine within the fish fat gradually decreased until it was the same as background levels,[136] indicating that bioaccumulation is reversible after the accumulating chemicals are removed. Sediment dwelling life forms also selectively accumulate low molecular weight compounds.[10]

Chlorinated phenols and guaiacols,[136, 138] chlorocymenes,[136] chlorinated veratroles,[139] chlorinated thiophenes,[105] and 1,1-dichlorodichloromethyl sulfone[140] have all been detected in fish taken from bleach plant receiving waters. The concentrations of these chemicals in samples taken away from the bleach plant was considerably less, or in some cases non-detectable.

Bioconcentration Factors. Another type of accumulation study is a controlled laboratory experiment in which bioconcentration factors (BCF's) are determined. The biocon-

centration factor is the ratio of the concentration of a test compound in the fat of the organism, to its mean concentration in the water over the test period. This test simulates what happens to fish in the receiving waters, but allows control of conditions. In these experiments, aquatic life forms (usually fish) are placed in water containing a specific concentration of a pollutant for a certain period of time.

Bioconcentration factors vary from near 1 to several hundred thousand for different components of bleaching effluents.[85] The same compound often has different BCF values for different test species, and also varies widely from lab to lab. Chlorinated veratroles, which are produced by bacterial action on phenolics,[141] have bioconcentration factors between 2000 and 30,000 depending on the number of chlorine substituents.[139] These BCF values are higher than those of the phenolics from which the veratroles are formed.

Both phenolics[138] and chlorinated thiophenes[105] are accumulated within fish that are exposed to the chemicals. However, after exposure ends the levels of these chemicals drop.

Environmental Persistence of Effluent Components

The persistence of a bleach plant effluent component is determined by how readily the material is degraded or transformed in waste treatment or in the receiving waters by biological or chemical means.

Degradation Of Effluent Components. Although the total quantity of AOX in mill effluents is decreased by post-mill effluent treatment processes such as aerated lagoons and

activated sludge treatment, all components of the effluent are not necessarily degraded equally.

Low (< 1000) molecular weight AOX is degraded to a greater extent than high molecular weight AOX by both alkali treatment and conventional biological treatment.[71, 72, 78, 125] However, biofilm treatment has the capability of degrading both high and low molecular weight AOX.[76] White rot fungus,[142] irradiation with visible light[143] and sunlight[82] all degrade high molecular weight effluent material.

Non-chlorinated compounds or naturally occurring components of the wood are more easily degraded than chlorinated compounds.[144, 145] Wood extractives, such as non-chlorinated resin and fatty acids, can be completely removed from effluents[144] and are generally removed by aerated lagoons and activated sludge systems with 80% or greater efficiency.[73, 98, 146]

Conventional biological treatment removes chlorinated phenolics to only a limited extent. About 30-50% removal is common for aerated lagoons[6, 72, 98, 103] and activated sludge systems.[6, 73, 145] Removal efficiency for mono- and dichlorinated phenolics is greater than for the tri- and tetrachlorinated compounds, which may be removed to as small an extent as 20% or less[72, 145] or may not be removed at all.[103] Therefore, a high proportion of extensively chlorinated phenolics can be present in treated mill effluents.[147]

Alternative methods for the removal of chlorinated phenolics exist, including ultrafiltration in combination with aerobic fungal treatment,[148] combination anaerobic/aerobic treatment lagoons,[75] and laccase enzymes which polymerize phenolics and make them removable by flocculation.[149] The alternative methods remove more chlorinated phenolics than conventional methods (greater than 70% removal) and remove highly chlorinated phenolics as efficiently as the less chlorinated ones.

Most neutral compounds are readily degradable. Chloropropenals in effluents decompose upon storage.[109] Chloroacetones,[6] diterpenealdehydes,[98] and furfural, cymenes, dichlorobromomethane, and carbon tetrachloride[145] are all removed with greater than 60% efficiency by conventional effluent treatment. Chlorinated sulfones, on the other hand, are a class of neutral compounds that are degraded very little, and are found in treated effluents.[110, 134] Chloroform is removed by conventional treatment systems with an efficiency greater than 60%.[6, 72, 145]

Although compounds which are known to be toxic, such as chlorinated phenolics, are not completely removed from bleach plant effluents, in many cases the effluents are not lethal after biological treatment.[5, 6, 9, 33, 73] In addition, secondary treatment reduces chronic toxicity by about an order of magnitude.[9] Toxicity removal is probably highly dependent on operating conditions of the treatment system though, and in some cases toxicity is not completely removed.[98, 144]

Effluent treatment also entirely eliminates the mutagenicity of bleaching effluents.[6, 77, 121, 150] This is expected since most mutagenic compounds are readily degradable neutrals, and others such as MX undergo irreversible isomerization at neutral or higher pH, to compounds that are much less mutagenic.[151]

Transformations of Effluent Components. In most cases, effluent components are degraded to form more innocuous materials, as in biological treatment. However, persistent materials can be formed from more innocuous components. Among the transformations that can occur when effluents are discharged to the environment are chlorolignin degradation to chlorinated phenolic compounds,[61, 132] and dechlorination,[152] hydroxylation,[152] demethylation,[153] and methylation[61, 132, 139, 153, 154] of phenolics.

An example of the biological formation of more environmentally dangerous compounds from more innocuous ones is the formation of veratroles by methylation of phenolics. Veratroles are as toxic as guaiacols, but are less polar and more lipophilic. Therefore, they are more likely to bioconcentrate within the environment than guaiacols or phenols.[61, 139] Chlorinated veratroles have been isolated from fish taken from bleach plant receiving waters, but have never been found in bleach plant effluent[139] indicating that they are produced by bacterial activity or other post-treatment phenomena. Chlorinated phenolics and high molecular weight chlorolignin may be converted, by the aerobic activity of bacteria in the receiving waters, to methylated products such as chlorinated veratroles.[61, 132, 139, 141]

Acute Toxicity

Acute toxicity is measured by bioassays in which a test species (often fish or water fleas) is subjected to a specific toxin concentration for a specific period of time and the survival rate analyzed. The results of such tests are reported as LC_{50} values. The LC_{50} of a chemical is the concentration lethal to 50% of a population during the given test period. The LC_{50} values for toxic compounds in bleaching effluents range from about 1 mole/m^3 for succinic and benzoic acids, to between about 0.01 and 0.001 mole/m^3 for highly toxic effluent compounds such as 9,10-epoxystearic acid, chlorodehydroabietic acids, and tri- and tetrachlorophenols.[85] Another way to report the toxicity of bleach plant effluents is the toxicity emission factor (TEF) in which the amount and concentration of the effluent, and its LC_{50} are considered. The formula for the TEF is given below:

$$TEF = (CV)/LC_{50}$$

where

C = concentration of effluent
V = effluent volume per ton of pulp production
LC_{50} = concentration of effluent lethal to 50% of a test species population

The TEF, in effect, gives the volume of LC_{50} concentration effluent formed per ton of pulp production.

In some cases, based on LC_{50}'s, the (CD) stage effluent is more toxic than E stage effluent.[126, 127] Usually caustic extraction stage effluent is slightly more toxic than (CD) stage effluent based on LC_{50}'s because the E stage effluent is more concentrated. But based on TEF values, (CD) stage effluent is more toxic than the E stage effluent because the (CD) stage produces more effluent per ton of pulp.[98, 99, 106] Both debarking and black liquor evaporation wastes are more toxic than bleaching effluents based on LC_{50}'s, but have lower TEF values because of the low volumes of these streams.[98] Softwood bleaching effluents are more toxic than hardwood effluents.[98]

When ClO_2 substitution for chlorine is increased effluent toxicity may decrease,[29, 31, 38, 41, 96, 106, 155, 156] increase,[157] or remain unchanged.[33, 156] Results are dependent on the species used for the toxicity test, on bleaching conditions, and on whether the entire bleaching sequence or just the delignification stage effluents are considered. The toxicity of the total effluent is probably greater than just that of the delignification stages because of the possible substantial toxicity of the first chlorine dioxide brightening stage.[156] The true effect of ClO_2 substitution on toxicity remains unclear. However, at 100% ClO_2 substitution effluents can be non-toxic.[41, 96] At a given level of ClO_2 substitution in sequential addition, effluents are less toxic when Cl_2 is added first.[37] An increased final (CD) stage pH also decreases toxicity.[99]

Both oxygen bleaching[29, 53, 65, 106] and extended delignification,[65] which decrease the kappa number of the pulp before the (CD) stage, decrease acute toxicity. Less

lignin material must be removed and proportionately fewer toxic compounds are formed. The effluents are less toxic based on both LC_{50}'s and TEF values, because of the decreased effluent concentration brought about by these changes.

Bleaching effluent toxicity is not only caused by what is formed in the bleaching stages, but also by what is carried over into the stages. Any additional source of lignin entering the bleaching process will contribute to toxicity at least as much as residual lignin within the pulp. Black liquor and oxygen stage carryover to the (CD) stage[53, 58, 61] increase bleaching effluent toxicity. Black liquor carrover causes the same toxicity per kappa unit as residual lignin in effluents produced in the subsequent chlorine-based bleaching stages.[53, 61] Oxygen stage carryover causes more acute toxicity per kappa unit of oxygen stage carryover, in effluents from subsequent chlorine-based bleaching stages, than either black liquor carrover or residual lignin.[53, 61]

Mono- and dichlorodehydroabietic acid, and 9,10-epoxystearic acid are highly toxic extractives, and are found in E stage effluents.[158] However, extractives account for about 30% of the E stage effluent toxicity[158] and less than 20% of the overall effluent toxic load.[98, 126] Overall, extractives may play an insignificant role in total toxicity because of small amounts present.[99, 100]

Highly chlorinated compounds are generally more toxic than ones that are chlorinated to a reduced extent. Each additional chlorine substituted on phenolics increases acute toxicity.[101, 102] In fact, one of the most toxic compounds found in bleaching effluents is tetrachloroguaiacol.[158] Although phenolics can be highly toxic, only 10-15% of the (CD) stage toxicity, 30% of the total E stage toxicity,[98] and less than 50% of the overall effluent toxicity[98, 99, 102] can be explained by identified phenolics.

Chlorinated thiophenes are among the neutral compounds present in effluents, and are moderately toxic.[105] But chlorinated thiophenes are not present in effluents produced using well washed pulps,[93] since their precursors originate in the pulping process.

There is no significant relationship between acute toxicity and AOX,[7, 9, 10] or with individual compounds such as phenolics.[101] Furthermore, acute toxicity cannot be explained entirely by identified compounds and their toxicities.[98, 99, 102] However, acute toxicity is likely to be primarily due to the low molecular weight fraction of the effluent.[5, 83, 95, 101, 125, 126] Ninety-two percent of the (CD) stage toxic units and 75% of the E stage toxic units are contained in the first of two sequential ether extracts collected from the same effluents.[126] The phenolic and neutral components of the (CD) stage ether extract are highly toxic[126] and the acidic and phenolic components of the E stage effluent contain 80% of the E stage ether extract toxicity.[158]

Chronic Toxicity

The term chronic toxicity refers to the sub-lethal effects of chemicals on organisms. A chemical stress is applied to the test species and the effect on parameters such as egg hatching frequency or birth rate is determined.

Bleaching effluents may exhibit only slight chronic toxicity, and therefore the presence or absence of pulp bleaching effluents has little effect on the chronic toxicity of total mill effluents.[9] The level of AOX within effluents has no significant correlation with chronic toxicity.[9, 10]

Regardless of whether bleaching effluents are significant contributors to overall mill effluent chronic toxicity, the chronic toxicity of bleaching effluents can be decreased by a number of methods. Increased ClO_2 substitution for chlorine,[8, 35, 96] decreased

atomic chlorine charge,[8] addition of chlorine first in sequential chlorine/chlorine dioxide bleaching,[35] and a decreased pulp kappa number before the (CD) stage[8, 96] are all likely to decrease chronic toxicity. As was the case with effluent lipophilicity and acute toxicity, additional chlorine substituents on phenolic compounds, increase the chronic toxicity of the compounds.[134]

Algae Toxicity

Chlorate ion is formed as a byproduct of ClO_2 delignification, and is toxic to brown algae.[29, 61, 159] Chlorate formation increases as ClO_2 substitution for chlorine increases.[31, 33, 61] In fact, chlorate formation increases linearly with the applied ClO_2 charge.[30, 160] When bleaching with both chlorine and chlorine dioxide, addition of chlorine dioxide first decreases chlorate levels.[37, 61, 161] Chlorate formation is also decreased by a lower kappa number pulp entering the (CD) stage, because less ClO_2 is applied.[54] Fortunately, chlorate can be efficiently removed from effluents by conventional effluent treatment,[33] and anaerobic effluent treatment completely eliminates chlorate.[74, 80]

Mutagenicity

Mutagenicity refers to the ability of a compound or mixture of compounds to induce genetic changes in organisms. Mutagenicity tests are done by the Ames test, in which microorganisms are subjected to chemicals, and the number of mutants counted and compared to a control case.

Untreated (CD) stage effluent exhibits mutagenic behavior[32, 121, 150, 162, 163] while effluents from other stages do not.[32, 162, 163] A decrease in the amount of lignin entering the (CD) stage decreases mutagenicity. For example, a lower pulp kappa num-

ber before the (CD) stage[53] and decreased carryover due to improved pulp washing,[58] both decrease mutagenicity. Mutagenicity also decreases with a decreased molecular chlorine charge in the (CD) stage,[32] and is decreased by chlorine dioxide substitution for chlorine in the (CD) stage.[156]

Mutagenic effects are concentrated in the low molecular weight effluent fraction[162, 163] and the ether extractable fraction[107] of the (CD) stage effluent. Mutagenic activity is concentrated in the neutral fraction of the ether extract,[107] and in the least lipophilic fraction of the neutrals.[121] However, mutagenic activity is readily destroyed by alkali.[162, 163]

THESIS OBJECTIVE

The objective of this thesis research was to determine, in an environmentally relevant and comprehensive manner, the chemical composition of the organic material in pulp bleaching effluents produced by low-AOX bleaching. Such a characterization may provide an increased understanding of the extent to which effluents formed in different bleaching processes cause adverse environmental effects and may indicate which low-AOX process conditions minimize the potential for adverse environmental effects.

EXPERIMENTAL APPROACH

To achieve the thesis objective bleaching effluents were produced primarily by low-AOX bleaching processes and the effluents were characterized. The experimental approach that was taken, including aspects of the effluent characterization and pulp bleaching, is considered here.

EFFLUENT FRACTIONATION AND CHARACTERIZATION

The characterization methods used in this research included an effluent fractionation based on ether extraction and molecular weight distribution determination by gel permeation chromatography. These methods provided the environmentally relevant and comprehensive chemical characterization of the organic material in bleaching effluents.

Characterization was done on untreated effluents from individual bleaching stages. This provided more complete information about effluent composition than characterization of treated or combined stage effluents, since combining or treating effluents destroys or changes some material in them.

Ether Extraction Based Fractionation

Pulp bleaching effluents have been characterized with respect to adsorbable organic halide (AOX) content, and also in terms of individual compounds or environmentally significant groups of compounds such as chlorophenolics,[8, 27, 39, 53, 96, 99, 102, 104] chlorinated dioxins,[8, 114, 116] chlorinated neutral compounds,[96, 107, 113] chlorinated carboxylic acids,[96, 97] and chloroform.[27, 92] Because of the complexity of pulp bleaching effluents, these analyses give an incomplete picture of the likely environmental effects of

effluents. A preferable alternative is analysis of effluents by fractionation into meaningful classes of compounds, followed by relevant characterization of all fractions. Such an analysis includes all components of the effluent, not just compounds of special interest such as highly toxic or lipophilic compounds. This is important since the environmental behavior of effluents depends on the entire effluent, not on individual compounds. For example, acute effluent toxicity cannot be explained by identified compounds and the toxicities of these compounds.[98, 99, 102]

Ether extraction was chosen as the basis for effluent fractionation because virtually all effluent compounds known to be environmentally significant are found in ether extracts. The ether extract contains low molecular weight material[122, 126] which may correlate with toxicity,[5, 83, 125] and it exhibits the majority of the effluents toxicity[126] and mutagenicity.[107, 121, 163]

Since different classes of compounds differ in their likely environmental behavior, the ether extract was separated into acidic, phenolic, and neutral subfractions. Chlorinated acidic compounds,[97] chlorinated phenolics,[101, 104] and chlorinated neutral compounds[107, 109, 113] have all been isolated from the ether extracts of bleaching effluents and are all important from an environmental viewpoint. The acidic fraction contains some highly toxic compounds such as resin and fatty acids, and can exhibit a significant portion of the ether extract toxicity.[158] The phenolic fraction contains a variety of toxic phenolics[101, 102, 158] and is a highly toxic portion of the ether extract.[126] The neutral fraction is highly toxic[126] and contains the majority of the effluent's mutagenicity.[107, 121]

The ratio of chlorine to carbon (expressed as the number of chlorine atoms per 100 carbon atoms, Cl/C_{100}) was determined for the whole effluents and for all fractions. This ratio is environmentally significant since highly chlorinated compounds are generally more troublesome within the environment than those with fewer chlorine substituents. The Cl/C_{100} may predict the acute toxicity,[101, 102] chronic toxicity,[134] and

lipophilicity[133] of chlorinated phenolics. The lipophilicity for several classes of effluent compounds,[85, 105] increases as the Cl/C_{100} increases. Highly chlorinated phenolics[103, 145] are less degradable by biological treatment than phenolics with fewer chlorine substituents, and are therefore more likely to be discharged into the receiving waters. Non-chlorinated, naturally occurring compounds, such as resin and fatty acids, are more readily degradable than chlorinated compounds similar in structure.[98, 144, 145]

Effluent Fractionation Scheme

A fractionation scheme based on ether extraction was developed and applied to bleaching effluents. The fractionation was used to separate the effluents into 8 distinct fractions which differ from each other with regard to their potential for causing adverse environmental effects. Figure 5 depicts the effluent fractionation scheme, and Table VI lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted exhaustively with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions: a non-extractable fraction, and two ether extractable fractions. The first ether fraction was readily extracted material, and the second was removed slowly over an extended period. The first was further fractionated into acids, phenolics, and neutrals. Each fraction was then evaporated to remove ether (shown in Figure 5 by the dashed horizontal lines) to give the final samples on which the ratios of chlorine to carbon were determined. To account for the loss of volatiles, a sample of the whole effluent was similarly evaporated. Volatiles were determined by the difference between the whole effluent and volatiles-free whole effluent (non-volatile whole, NVW).

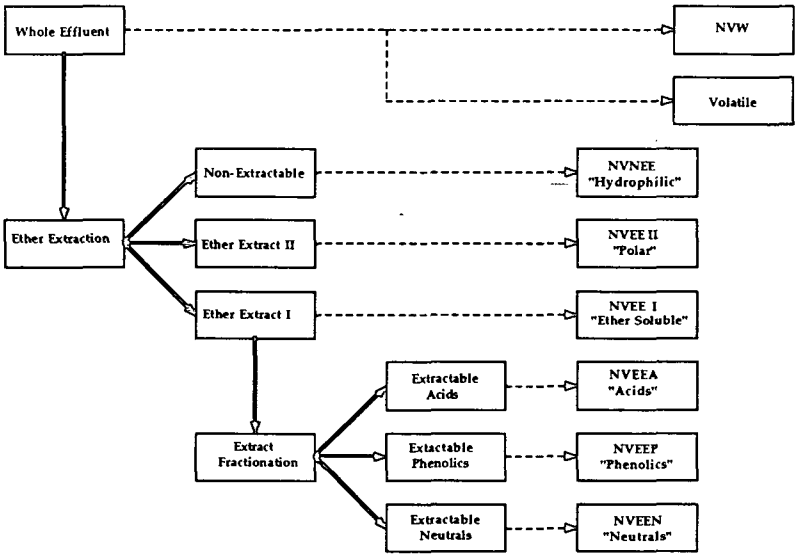

Figure 5. Effluent Fractionation Scheme.

Table VI. Effluent Fraction Codes and Descriptions of Fractions.

Fraction Code	Description
NVW	Non-volatile, whole.
NVNEE	Non-volatile, not extracted with ether ("Hydrophilic").
NVEE II	Non-volatile, difficult to extract with ether ("Polar").
NVEE I	Non-volatile, readily ether extractable ("Ether Soluble").
NVEEA	Non-volatile, ether extractable acidic compounds ("Acids").
NVEEP	Non-volatile, ether extractable phenolic compounds ("Phenolics").
NVEEN	Non-volatile, ether extractable neutral compounds ("Neutrals").

Molecular Weight Distribution Determination

Both ultrafiltration[88, 89, 127-131] and gel permeation chromatography[95, 131] have been used to determine the molecular weight distributions of pulp bleaching effluents. The molecular weight distribution is environmentally significant because low (< 1000) molecular weight material is more easily degraded biologically,[71, 72, 78, 125] and the quantity of low molecular weight material may correlate with environmental parameters such as acute toxicity.[5, 83, 125] High molecular weight material is less toxic[95, 126] and is not degraded as well by conventional effluent treatment.

Although molecular weight distributions may yield valuable information about the composition of effluents, a comparative determination of the molecular weight distributions of low-AOX bleaching effluents produced under well controlled conditions has not been done. In addition, results of molecular weight distributions have been unreliable due to the incomplete separation achieved by the methods used. Associations of molecules, dependent on effluent concentration, cause incomplete separation in the case of ultrafiltration.[108, 131, 132] Associations that occur in lignin-type substrates and cause problems in ultrafiltration, can be readily eliminated with gel permeation chromatography, by using a proper eluent system.[95, 164-166] But GPC has not often been used to determine the molecular weight distributions of bleaching effluents.

Previous GPC work has most often used ultraviolet (UV) detection.[45, 164-166] Although UV detection is appropriate for detecting lignin, it may not be appropriate for detecting bleaching effluents which may contain materials, including carbohydrates, that do not absorb UV as strongly as lignin or may not absorb at all. Results using UV detection are therefore biased toward strongly absorbing components of the effluent.

A method of aqueous gel permeation chromatography was developed and applied to the effluents produced in this research. The method utilized total organic carbon

(TOC) detection, which is a universal detection system for organic material, achieved improved low molecular weight separation compared to other similar GPC systems, and eliminated association.

PULP BLEACHING CONDITIONS

The chemical composition of the organic material in effluents from low-AOX bleaching processes was determined using these environmentally relevant characterization methods. Different bleaching sequences that decrease AOX discharge and process conditions within the bleaching sequences were investigated.

Bleaching Processes

Among the methods most likely to be implemented in the near future to decrease AOX discharge, are the use of oxygen, both in delignification and in oxidative extraction, and high levels of chlorine dioxide substitution for chlorine. These are well established technologies and are already widely used. The use of oxygen in caustic extraction is an inexpensive technology to implement for decreasing AOX, and oxygen delignification offers chemical cost savings in addition to environmental benefits. Chlorine dioxide is a highly effective bleaching agent which is already widely used and is likely to be expanded to 100% substitution for chlorine as a means of environmental improvement and for decreasing AOX levels. The use of 100% chlorine dioxide is considered an "ECF" or "elemental chlorine-free" process, which in today's environmentally conscious society can be used as a marketing tool.

A comparison of the effect of 100% chlorine dioxide substitution and the effect of oxygen bleaching on the effluent characteristics was done. Effluents from 100% chlorine

dioxide bleaching of an oxygen delignified pulp were compared to those from 100% chlorine bleaching of the same pulp, and effluents from 100% chlorine dioxide bleaching of both oxygen delignified and unbleached pulps were compared. Oxygen enhanced caustic extraction followed each C or D stage.

Process Conditions

The OD(EO) partial sequence is part of a full bleaching sequence that is likely to be extensively implemented to decrease AOX levels. Initial D stage pH and D stage reaction time in the OD(EO) partial sequence were varied, and the effluents produced under these different conditions were characterized. Since the formation of chlorinated organics occurs in the D stage, only the D stage process conditions were varied.

The reaction time in the D stage is expected to affect effluent composition in a different manner than it affects delignification, since oxidation by chlorine dioxide delignifies the pulp, while reaction with chlorine or hypochlorous acid, formed as byproducts of chlorine dioxide oxidation,[167] can produce AOX. These separate processes may have separate time dependence.

In chlorine dioxide bleaching, the pH has an impact on the chemical species present[167] and should therefore have an impact on the composition of the organic material in the bleaching effluents and on delignification. Fewer chlorinated phenolics[99, 100, 102] and fewer chlorinated dioxins[114, 116] are formed at increased pH levels in the (CD) stage. Increased delignification may be achieved at decreased pH levels with 100% chlorine dioxide.[36]

RESULTS AND DISCUSSION

The Results and Discussion consists of three parts: The first part describes the organization the Results and Discussion. The second part presents the results of the ether extraction based effluent fractionation experiments. The third part presents the results of the gel permeation chromatography experiments.

ORGANIZATION

The Results and Discussion consists of 7 sections in addition to this organization section. Five of these sections are papers that have been presented at conferences and have appeared in the conference proceedings. In some cases the papers have been subsequently submitted to journals. References appear at the end of each paper and figures and tables are numbered sequentially from the beginning of that particular paper. In sections not written as papers, references are included in the Literature Cited section of the thesis, and figures and tables are numbered from the beginning of the thesis.

Ether Extraction Based Fractionation

This part of the Results and Discussion consists of 5 sections, 3 of which are written as papers. Section 1 and Section 2 discuss preliminary investigations of the AOX method and the ether extraction procedures. Sections 3-5 present the actual fractionation and characterization data for effluents produced during this research. These sections all implement ether extraction of effluents, fractionation of the extracts into acidic, phenolic, and neutral subfractions, and the determination of chlorine to carbon ratios.

Section 3, entitled "Characterization of Effluent Fractions from ClO_2 and Cl_2 Bleaching of Unbleached and O_2 Bleached Softwood Kraft Pulps," considers the effect of 100% chlorine dioxide substitution and oxygen bleaching on the composition of the effluents. It was originally presented at the 1993 TAPPI Pulping Conference. This section is a condensed version, prepared as a manuscript for publication in *Tappi Journal*. The more complete Pulping Conference version of this paper, which contains data for all effluent fractions, is included in Appendix 1.

Section 4, entitled "The Effect of D Stage pH on Effluent Quality: Characterization of Effluent Fractions from OD(EO) Bleaching of Softwood Kraft Pulp," considers the effect of initial D stage pH on the effluent composition. It was originally presented at the 1994 Annual Meeting of the Technical Section of the CPPA. This is again a condensed version, prepared as a manuscript for publication in the *Journal of Pulp and Paper Science*. This version contains more accurate explanations of the results than the more complete CPPA Conference Proceedings version of the paper, which is included in Appendix 2. The Appendix 2 version of this paper contains data for all effluent fractions.

Section 5, entitled "The Effect of D Stage Reaction Time on the Characteristics of Whole Effluents and Effluent Fractions from D(EO) Bleaching of Oxygen Delignified Softwood Kraft Pulp," considers the effect of D stage reaction time on the composition of the effluent. It was presented at the 1994 International Pulp Bleaching Conference.

Gel Permeation Chromatography

This part of the Results and Discussion consists of 2 sections. One considers the preliminary development of the gel permeation chromatography method and the other applies the method to the effluents produced during this research.

Section 6, entitled "Development of a Method of Aqueous Gel Permeation Chromatography for the Determination of Molecular Weight Distributions of Bleaching Effluents," describes the preliminary GPC method development, and contains molecular weight distributions for mill-produced bleaching effluents. This paper was presented at the 1994 International Environmental Conference.

Section 7, entitled "Molecular Weight Distributions of Effluents from Chlorine Dioxide Delignification," compares all the bleaching effluents produced during this research, with regard to molecular weight distribution. It was accepted for presentation at the 1994 TAPPI Pulping Conference.

ETHER EXTRACTION BASED FRACTIONATION

This portion of the Results and Discussion consists of 5 sections. The first 2 sections consider AOX method development and preliminary ether extraction studies. Sections 3-5 provide the actual experimental results of this portion of the research. These 3 sections apply the ether extraction based effluent fractionation scheme and characterization to bleaching effluents that have been produced using low-AOX bleaching conditions.

Section 1: AOX Method Development and Validation

Section 1 is a compilation of the AOX method development and validation experiments that were done during the course of the ether extraction based fractionation experiments. The shaker or batch AOX method[13, 14, 15, 16] was used in this research because it is more appropriate for samples that contain precipitates, as several effluent fractions do. The other AOX method (the column method) requires the removal of any solids, including precipitates, before sample preparation.[13-15]

A major objective of these experiments was minimization of "breakthrough" or non-detection of AOX due to incomplete adsorption by the activated carbon. Breakthrough was not initially known to be a concern, but during the course of AOX determinations in this work suspicions arose regarding substantial AOX breakthrough with 100% ClO_2 bleaching effluents. Breakthrough was determined by adsorption of samples with sequential batches of carbon (sequential adsorptions).

These experiments led to improved AOX measurements over the course of experimentation and to more accurate results. They also demonstrated the impact that the AOX method had on the accuracy of experimental results.

AOX breakthrough was different for effluents produced by different bleaching sequences, and could be 10% or more for effluents produced by 100% ClO_2 bleaching. Breakthrough was minimized by use of additional activated carbon or by employing additional sample shaking time. After the completion of these experiments, non-detection of AOX in 100% ClO_2 effluents was minimized by the implementation of 2 sequential carbon adsorptions.

Statistical Analysis

To determine significant effects, analysis of variance was done on the AOX and breakthrough results. In this analysis replicates were not true replicates, since new sample dilutions were not prepared for each AOX sample. However, dilution of effluent samples was done with volumetric pipettes and flasks, and samples were well mixed before the dilution aliquot was removed. Therefore, this effect was minimal compared to other sources of variation in sample preparation and measurement. Larger sources of variation may include the sample dilution water, carbon and filter contamination, and carbon loss throughout the sampling process.

AOX Calibration

Detection by the microcoulometric titration cell is assumed to be linear and only a single standard, containing 20 μg of AOX, is normally run to verify sample recovery.[13-17] This practice was tested using trichlorophenol standard solutions.

Samples containing between 4 and 28 μg AOX were prepared and tested. Each sample was shaken for 1 hour with 80 mg of activated carbon, according to the Scandinavian AOX method.[16] The resulting calibration curve is shown in Figure 6. A linear relationship existed even beyond 20 μg, which was the maximum concentration of AOX in any determination during normal operation. The regression line is given at the top of the figure.

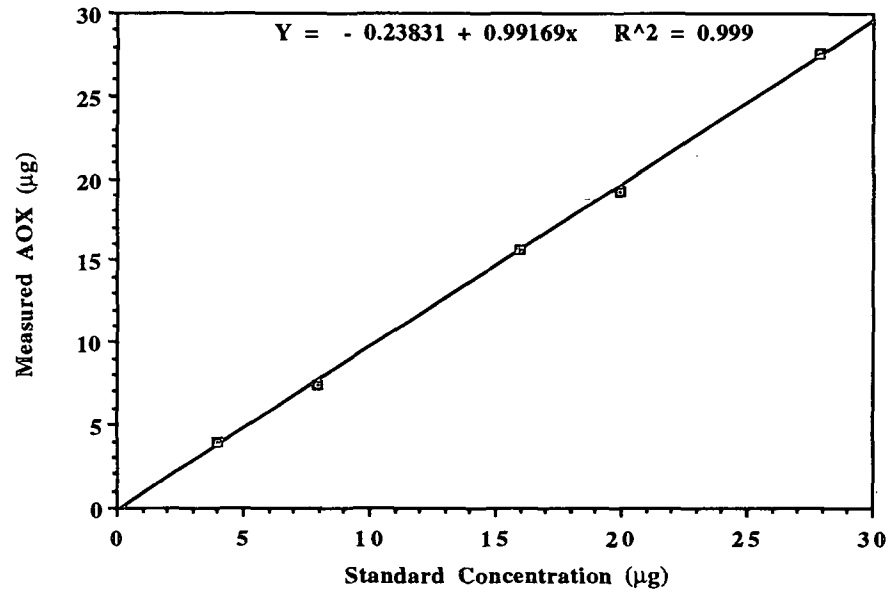

Figure 6. AOX Calibration Curve. (AOX conditions: batch method, 80 mg activated carbon, 1 hour shaking time, single adsorption)

Blank, Standard, and Mill Effluent Shaking Time Effects

The effect of shaking time on the measured level of AOX was determined for an AOX method blank, a trichlorophenol standard solution, and for solutions of mill (C+D) and E stage effluents produced using a high percentage of chlorine as the bleaching agent. In this group of experiments, 80 mg of activated carbon per sample was used

The results of these experiments are shown in Figures 7 and 8. No time related trend was seen for any samples. However, several of the blanks and E stage effluent samples were significantly different than others. In the case of the blank this can be attributed to random variation in the blanks from day to day. For example, AOX in the water source varied widely, resulting in a higher or lower blank value. Variation in E stage AOX was possibly due to degradation of the AOX in the effluent dilution. At the

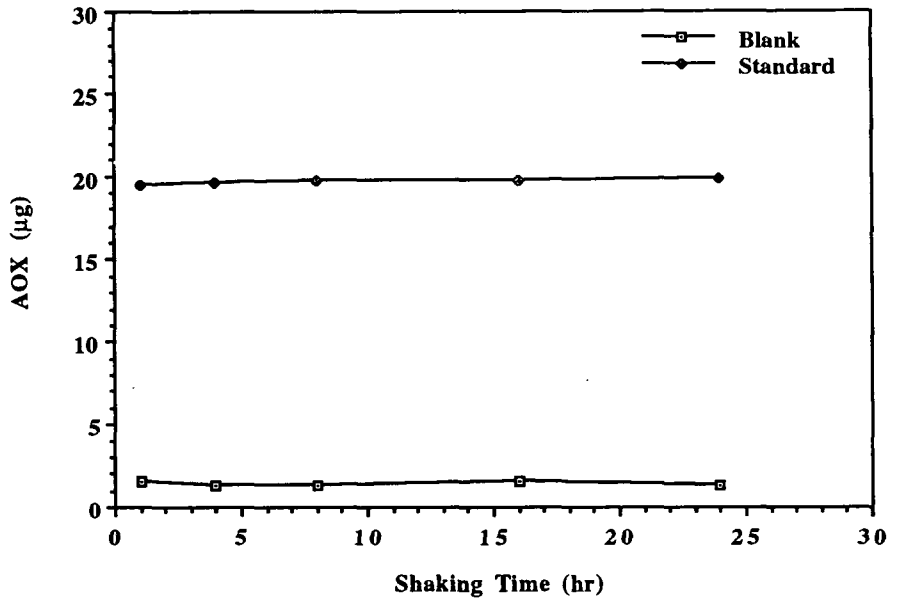

Figure 7. Effect of Shaking Time on Determined Blank and Standard AOX. (AOX conditions: batch method, 80 mg activated carbon, variable shaking time, single adsorption)

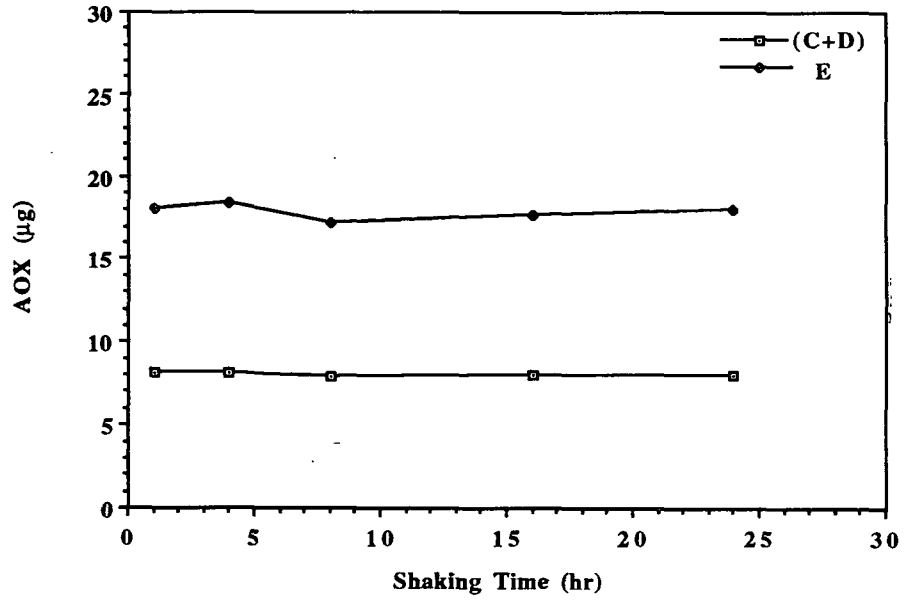

Figure 8. Effect of Shaking Time on Determined Mill Effluent AOX. (AOX conditions: batch method, 80 mg activated carbon, variable shaking time, single adsorption)

time of these experiments, a fresh dilution was not prepared before each use, and sample degradation was possible as the diluted sample aged.

Although no time related trend was observed with these samples, shaking time was increased to 4 hours for subsequent analysis work. The modified AOX method, using 80 mg of activated carbon and 4 hours of sample shaking time, was used during parts of the ether extraction based effluent analyses (those appearing in Sections 3 and 4). Additional shaking time was implemented to insure more complete adsorption of chlorinated organics in polar effluent fractions such as the NVNEE and NVEEA fractions.

Breakthrough for Different Effluent Types

During effluent analysis experiments incomplete adsorption of effluents produced by 100% ClO_2 bleaching became apparent, and experiments were done to determine the extent of the problem. In these experiments, sequential adsorptions were done on the same sample and the AOX of each batch of carbon was determined. AOX samples were prepared as usual and after initial filtration the filtrates were treated with a second batch of activated carbon (second adsorption). Any detected AOX in the second adsorption indicated incomplete adsorption in the first, and is referred to as "breakthrough".

The percentage of AOX breakthrough was compared for dilutions of laboratory produced effluents, from the D or C, and (EO) stages of OD(EO), OC(EO), and D(EO) bleaching. These data were collected using 80 mg of activated carbon and 4 hours of sample shaking. The NVW effluent fraction (volatiles-free whole effluent) from each bleaching sequence was used.

The results are shown in Figure 9. The OD(EO) sequence had the highest percentage breakthrough and the OC(EO) sequence had the lowest for both stages. Effluents

produced using chlorine contain more highly chlorinated, non-polar organics, and are likely to be adsorbed more completely by the carbon.

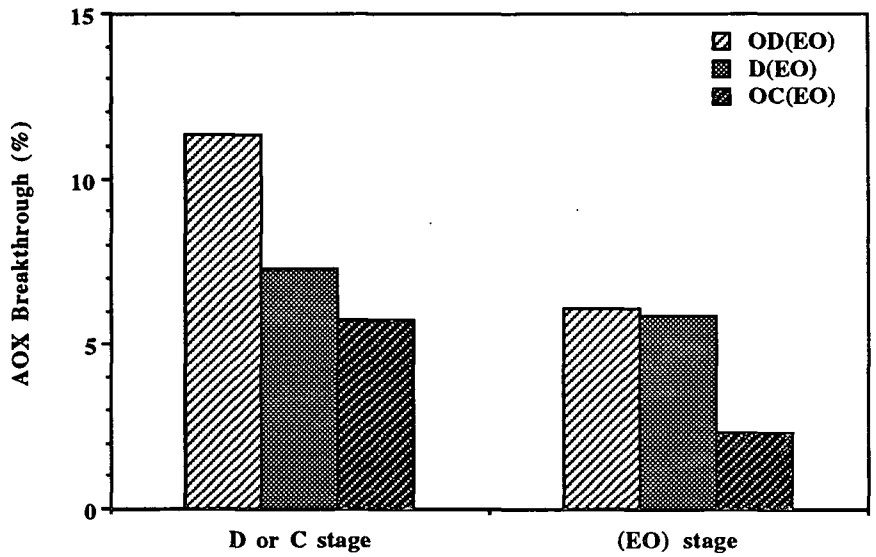

Figure 9. Breakthrough for Different Effluent Types. (AOX conditions: batch method, 80 mg activated carbon, 4 hours shaking time, double adsorption)

Activated Carbon and Nitrate Ion Addition Levels

Increased levels of activated carbon addition has been shown to increase the quantity of determined AOX.[130] Activated carbon addition level and nitrate ion addition level were compared with respect to breakthrough minimization.

Double Adsorption AOX and Breakthrough Determination. The D stage NVW effluent was used, since it had the highest level of breakthrough in the previous experiments. Four hours of sample shaking was done in all cases, and the normally used 80 mg

of activated carbon was compared to 120 mg, and to 120 mg with 10 times the normal nitrate ion concentration.

The double adsorption AOX results for the dilution of the OD(EO) sample are shown in Figure 10. Total AOX is given by the sum of both AOX batches. When 120 mg of carbon was used rather than 80 mg, the adsorption-1 AOX increased. When the nitrate ion concentration was increased, the adsorption-1 AOX decreased. The adsorption-2 AOX remained relatively constant under all conditions. Total AOX was increased when 120 mg of activated carbon was used per batch, and decreased when extra nitrate was added.

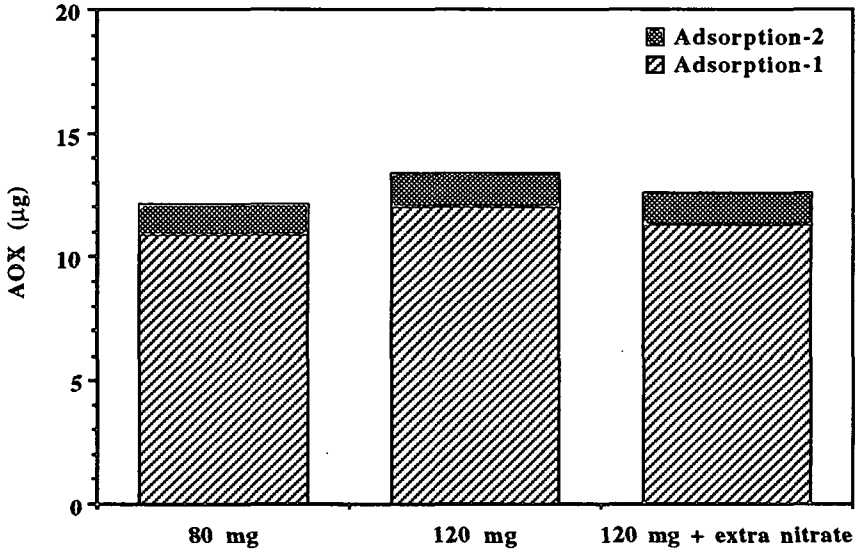

Figure 10. Double Adsorption AOX Determined Under Different Conditions. (AOX conditions: batch method, variable activated carbon level, 4 hours shaking time, double adsorption)

The percentage of AOX breakthrough for each set of conditions is given in Figure 11, and did not change. Breakthrough refers to the adsorption-2 AOX expressed as a percentage of the total AOX.

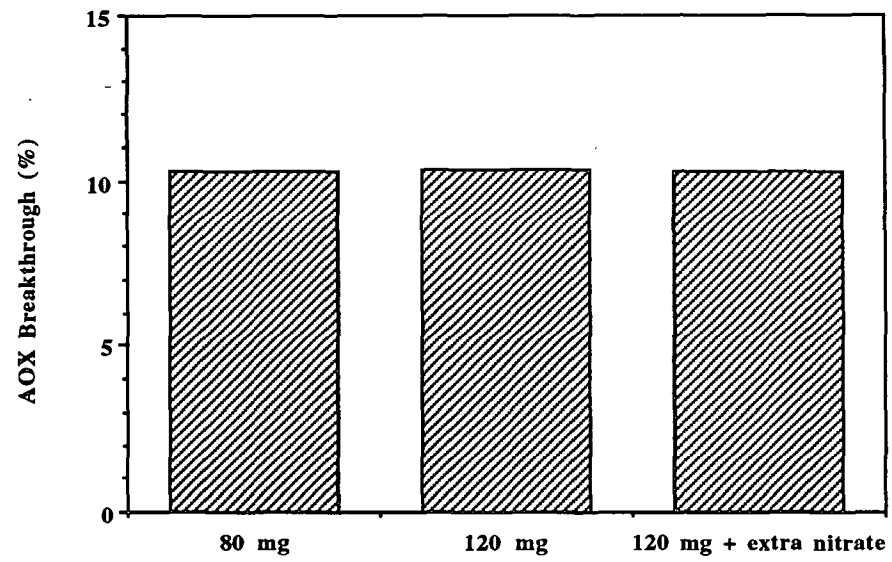

Figure 11. Breakthrough Determined Under Different Conditions. (AOX conditions: batch method, variable activated carbon level, 4 hours shaking time, double adsorption)

Triple Adsorption AOX and Breakthrough Determination. A third AOX adsorption was done to determine if breakthrough could occur even beyond 2 adsorptions. The whole OD(EO) effluent was used and shaking time was 4 hours. In this set of experiments 80 mg, 120 mg, and 160 mg of activated carbon addition were compared.

Figure 12 shows the results of the triple adsorption AOX analysis. Total AOX remained about constant for the 3 sets of conditions. However, the mean adsorption-1 AOX increased when 120 or 160 mg of carbon was used. Mean adsorption-2 and 3 AOX were simultaneously reduced, maintaining the relatively constant total AOX.

The breakthrough results are given in Figure 13. Adsorption-2 breakthrough refers to adsorption-2 AOX expressed as a percentage of the sum of the adsorption-1 and adsorption-2 AOX. Adsorption-3 breakthrough refers to adsorption-3 AOX expressed as a percentage of the sum of all 3 AOX adsorptions. Mean adsorption-2 and adsorption-3 breakthroughs were decreased when 120 or 160 mg batches of carbon were used. However, these apparent differences were not large enough to be considered statistically significant. When 120 mg or more carbon was used, the adsorption-3 breakthrough was decreased to near 2% of the total AOX. This indicates that under appropriate conditions, adsorption-3 breakthrough can be limited to an acceptable and insignificant level.

In subsequent experimentation, double column adsorption with 120 mg of activated carbon was used because this method increased the level of detected AOX and decreased the mean breakthrough level. The triple adsorption system was not further used because it was not a practical alternative considering the minor levels of AOX that remain undetected after 2 adsorptions. Carbon addition levels greater than 120 mg were not used after these experiments, because this was too much carbon to be conveniently filtered or to fit into the AOX sample boat without the chance for considerable loss. It also represented no reduction in breakthrough compared to 120 mg of carbon.

Double Adsorption/Double Column Comparison

A comparison of the double column method[13-15] and the double adsorption shaker method was done. The column method employs 2 carbon packed cartridges in series through which the sample solution is passed. The cartridges are then rinsed with nitrate solution to wash away any chloride ion. The same unfiltered sample dilutions were used to achieve a direct comparison of the double adsorption shaker method and the double column method. In this experiment, 4 hours of shaking time and 120 mg of acti-

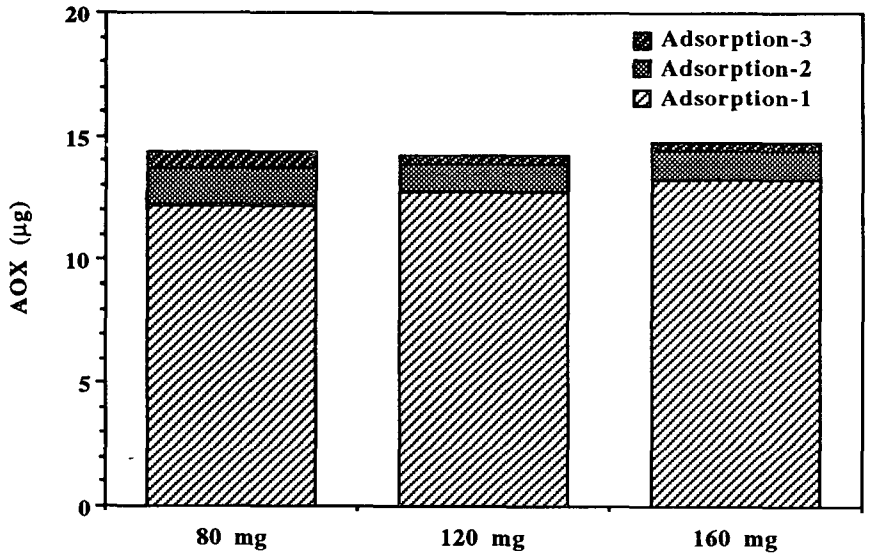

Figure 12. Triple Adsorption AOX Determined Under Different Conditions. (AOX conditions: batch method, variable activated carbon level, 4 hours shaking, triple adsorption)

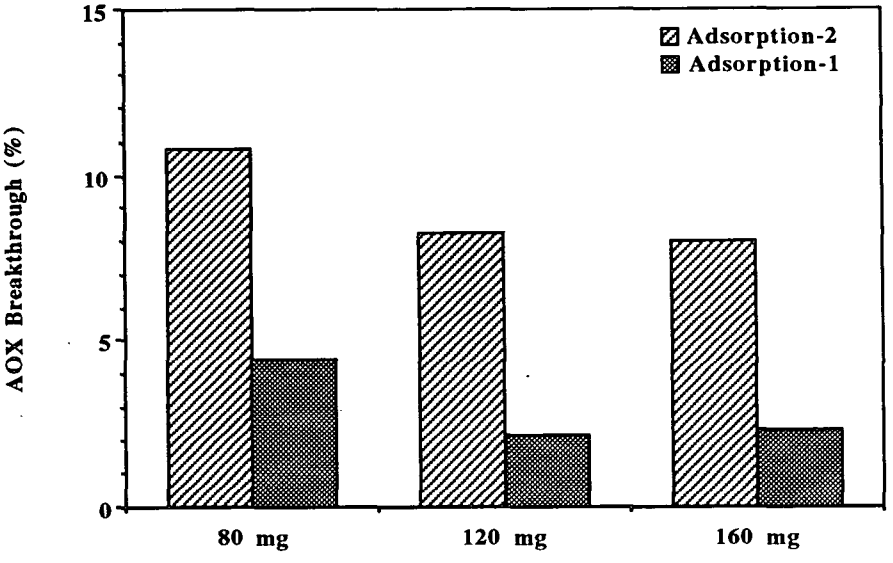

Figure 13. Double and Triple Adsorption Breakthrough Determined Under Different Conditions. (AOX conditions: batch method, variable activated carbon level, 4 hours shaking time, triple adsorption)

vated carbon per batch were used for the shaker method. The lab produced whole D and (EO) stage effluents from OD(EO) bleaching were tested in this set of experiments.

The AOX results for this comparison are shown in Figure 14. Adsorption/column-1 D stage AOX was the same for both methods, but adsorption/column-1 (EO) stage AOX was greater for the shaker method. Adsorption/column-2 D and (EO) stage AOX was greater for the column method. Total D stage AOX was greater for the column method but total (EO) stage AOX was the same for both methods. Similar results have been obtained by researchers at Paprican, who found that the column method gave higher determinations for C stage effluents but similar results for E stage or combined effluents.[78, 130]

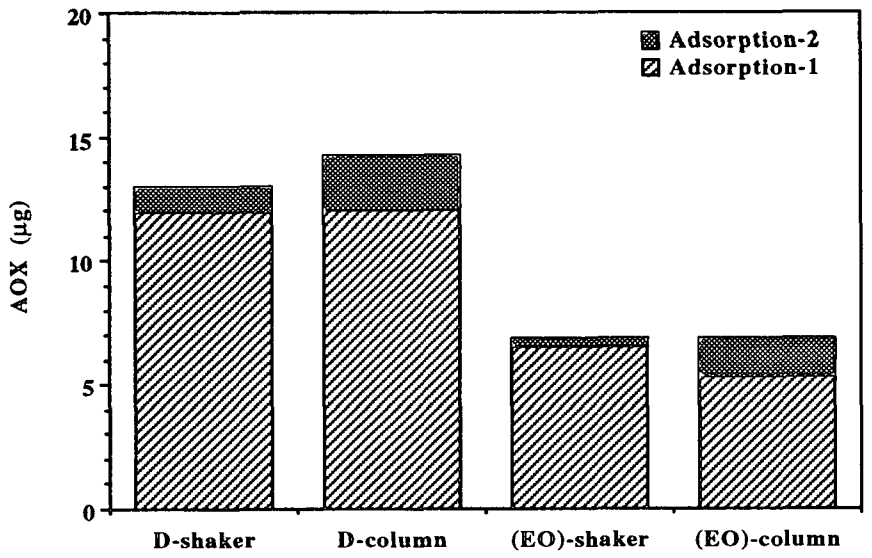

Figure 14. Comparison of Determined AOX for the Double Adsorption Shaker Method and Double Column Method. (AOX conditions: batch and column methods, 120 mg activated carbon per batch, 40 mg activated carbon per column, 4 hours shaking time for the batch method)

The breakthrough results are shown in Figure 15. Because of the increased column-2 AOX determined by the column method, breakthrough was much greater for the column method. For effluents from both stages, breakthrough was more than 15% when the column method was used. This level of breakthrough is not considered acceptable based upon standard methods.[13-15]

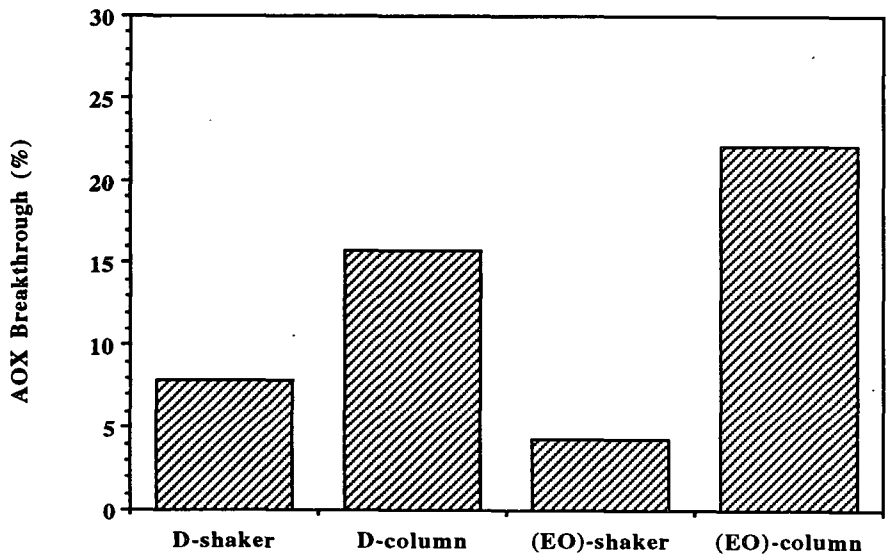

Figure 15. Comparison of Breakthrough for the Two-Batch Shaker and Column Methods. (AOX conditions: batch and column methods, 120 mg activated carbon per batch, 40 mg activated carbon per column, 4 hours shaking time for the batch method)

Shaking Time Effects with Lab Produced OD(EO) Effluents

The effect of shaking time on AOX determination and breakthrough was again considered, this time using lab produced D and (EO) stage effluents from OD(EO) bleaching. Double adsorption AOX determination with 120 mg of activated carbon per batch was used, and samples were shaken for either 1 or 4 hours.

The double adsorption AOX results are shown in Figure 16. Total AOX was not affected by shaking time. However, a decreased level of adsorption-1 AOX was determined with 1 hour of shaking time, for both the D and (EO) stage effluents. A simultaneous increase in adsorption-2 AOX levels, resulted in the approximately equal total AOX.

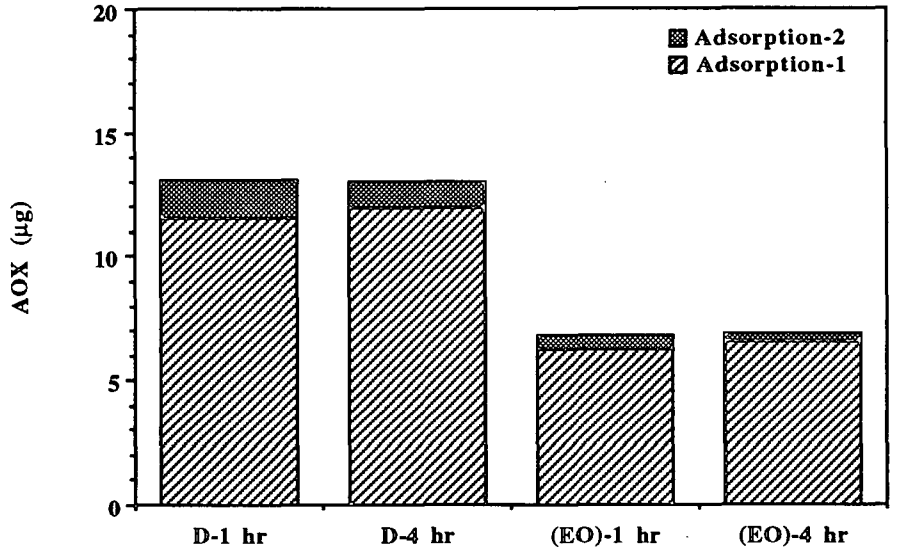

Figure 16. Effect of Shaking Time on Determined Double Adsorption AOX. (AOX conditions: batch method, 120 mg activated carbon, variable shaking time, double adsorption)

Breakthrough results are shown in Figure 17. With 1 hour of shaking, the adsorption-2 AOX was greater and therefore the breakthrough was also greater. Because overall AOX was equivalent using the 2 levels of shaking time, 1 hour of shaking was used in subsequent experiments with the double adsorption AOX system, based primarily on practical time considerations. The double adsorption system using 4 hours of shaking per batch required an unrealistic 8 hours of shaking per sample.

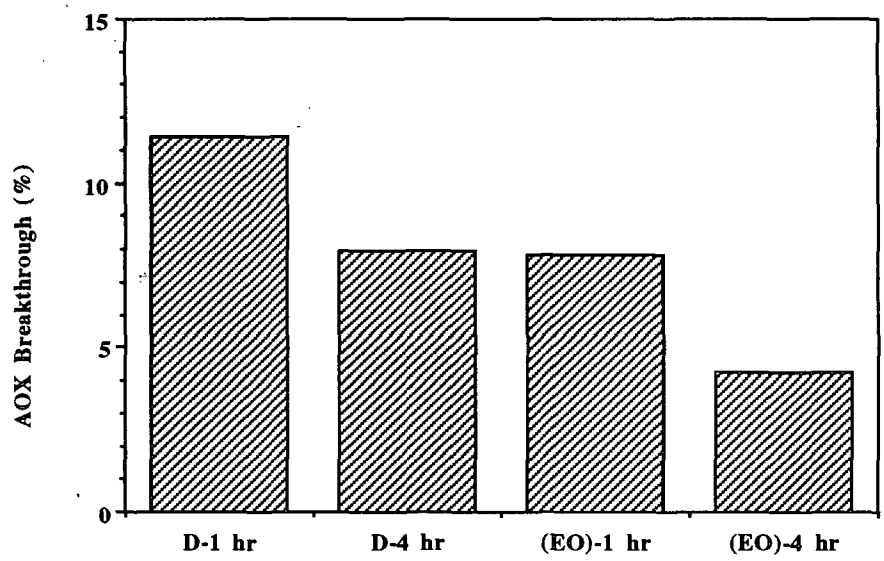

Figure 17. Effect of Shaking Time on Breakthrough. (AOX conditions: batch method, 120 mg activated carbon, variable shaking time, double adsorption)

Breakthrough for Different Effluent Fractions

Breakthrough for all OD(EO) effluent fractions was determined using the double adsorption AOX system. One hour of shaking and 120 mg of activated carbon per batch were used.

Figure 18 shows the breakthrough data for all D and (EO) stage fractions. Breakthrough was generally less for all (EO) stage fractions. The NVNEE fraction was the exception. Mean breakthrough was less for NVW effluents compared to whole effluents, suggesting that a large part of the breakthrough may be due to volatile compounds. Polar fractions (NVNEE, NVEEA) had greater breakthrough than more non-polar fractions (NVEE I, NVEEP, NVEEN), as expected.

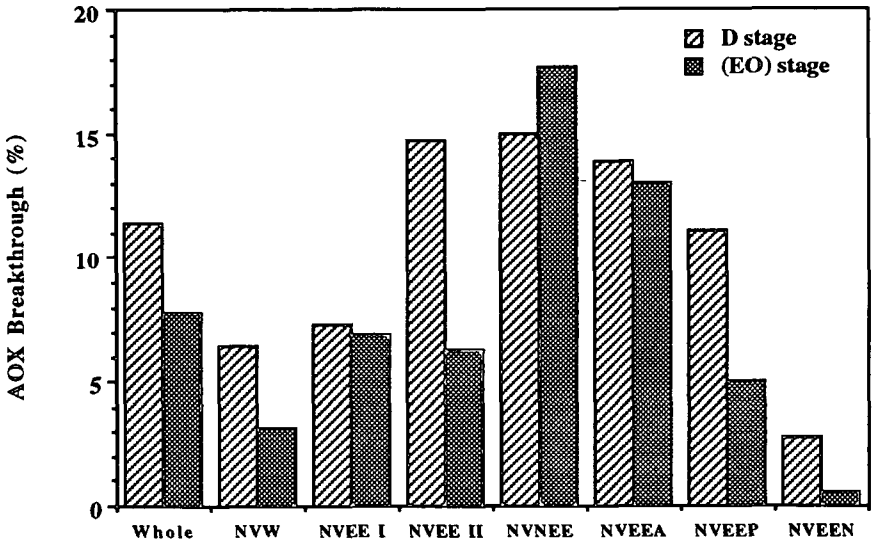

Figure 18. Breakthrough for Different Fractions of OD(EO) Bleaching Effluents. (AOX conditions: batch method, 120 mg activated carbon, 1 hour shaking time, double adsorption)

Implications of AOX Method for Interpretation of Experimental Results

Only during effluent fractionation and characterization work did problems with the accuracy of AOX determinations on 100% ClO_2 effluents become apparent. Improvement in the AOX method was continual, and therefore several modifications of the AOX method were used during this research. Effluent characterization results may be somewhat affected, depending on the method used.

During the first 2 groups of characterization experiments - the comparison of effluents from OD(EO), OC(EO), and D(EO) bleaching sequences (Section 3) and the comparison of initial D stage pH within the OD(EO) sequence (Section 4) - a slight modification of the Scandinavian shaker method[16] was used. Rather than shaking samples for

only 1 hour, 4 hours of shaking time was done to allow further adsorption of polar materials.

Comparisons of Cl/C_{100} are valid for 100% ClO_2 effluent fractions because the level of breakthrough was relatively constant within a given fraction. Because of breakthrough, all Cl/C_{100} values were low by an approximately equivalent amount.

However, breakthrough probably affected the results of the comparison of 100% Cl_2 and 100% ClO_2 bleaching more. Because effluents and effluent fractions from 100% Cl_2 bleaching are more non-polar, breakthrough was decreased compared to the ClO_2 effluents and fractions, and the Cl/C_{100} values for 100% Cl_2 effluents and fractions were higher than if breakthrough was constant. Since the differences between the Cl/C_{100} values for 100% Cl_2 and 100% ClO_2 effluent fractions were very large, the error due to breakthrough does not change the conclusions of this portion of the research.

After all AOX method development and validation experiments were done, the optimized method was used. This optimized method (double adsorption AOX system, using 120 mg of activated carbon per batch and 1 hour of sample shaking per batch) was applied to effluents produced during the comparison of D stage reaction time within the OD(EO) bleaching sequence (Section 5). Determined Cl/C_{100} values should be increased using this AOX method compared to the earlier method, and the results should more accurately reflect the actual ratio of chlorine to carbon within the effluents and effluent fractions.

Section 1 Conclusions

These experiments led to improved AOX measurements over the course of experimentation and to more accurate results. They also demonstrated the impact that the AOX method had on the accuracy of experimental results.

AOX breakthrough was different for effluents produced by different bleaching sequences, and could be 10% or more for effluents produced by 100% ClO_2 bleaching. Breakthrough was minimized by use of additional activated carbon or by employing additional sample shaking time. After the completion of these experiments, non-detection of AOX in 100% ClO_2 effluents was minimized by the implementation of 2 sequential carbon adsorptions.

Section 2: Preliminary Ether Extraction And Extract Fractionation Studies

Section 2 is a compilation of preliminary ether extraction and extract fractionation studies. The results were important to the development of the ether extraction based effluent fractionation scheme, and for validation of the fractionation methods. They also indicated how certain variables affected the fractionation process.

Material extracted by ether, from effluents, during an initial short extraction period, was much more concentrated in organic chlorine than either the whole effluent itself or the material extracted at longer times. The fractionation scheme, including 2 distinct ether extract fractions, was developed as a result of the strong dependence of ether extract organochlorine concentration on extraction time.

No significant quantity of TOC was detected in any effluent fraction when deionized water was extracted with ether. Highly polar model compounds were poorly extracted by ether, and poorly detected by the AOX method. Phenolic compounds partitioned predominantly into the phenolic fraction, but some phenolic material was lost during sample evaporation. However, far more phenolic material was recovered in this research than in previous research.

Different ether extractors removed different amounts of material from effluents during the immediate short extraction interval, but removed similar amounts of material during a second consecutive, longer term extraction period. The overall level of removed material (total of both extraction periods) did not differ.

Effect of Extraction Time on Extract Content

The effect of extraction time on the quantity of extracted TOC was considered. This preliminary investigation used a 1 L liquid-liquid extractor. A mill produced (C+D) stage effluent was extracted for different lengths of time between 6 and 96 hours. This resulted in 157-269 mg TOC in the ether extract, as shown in Figure 19. A very short period of extraction removed a considerable amount of TOC from the effluent, yet removal continued throughout. The level of removal approached an asymptotic level at very long extraction times.

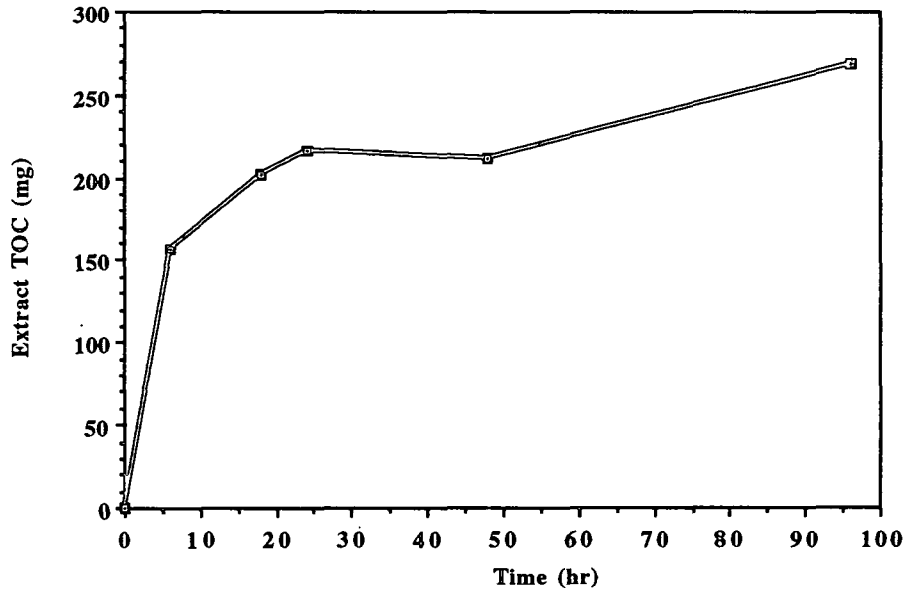

Figure 19. Extracted TOC for Different Length Extraction Periods.

Both mill produced (C+D) and E stage effluents were extracted, again using the 1 L extractors, and 3 separate ether extract phases were taken, corresponding to different extraction periods. The first ether phase consisted of material removed from the effluent

within the first 50 hours, the second consisted of material removed between 50 and 250 hours, and the third consisted of material removed between 250 and 322 hours of extraction. After each interval of extraction, the extract was removed and replaced with fresh ether for the subsequent extraction.

The ratio of chlorine atoms per 100 carbon atoms (Cl/C_{100}) was determined for each ether fraction and are compared to those of the whole effluents in Figure 20. The first ether extract had a higher Cl/C_{100} than the whole effluent for both the (C+D) and E stages. This supports the contention that the ether extractable material is a fraction of environmental significance, since it contained the most highly chlorinated material. The Cl/C_{100} of the second and third ether extracts differed considerably from the first, but were very similar to one another for both stages. Although the second and third ether phases had lower Cl/C_{100} values than the whole effluents, they could still be of environmental importance since ether extracts contain low molecular weight material.[126]

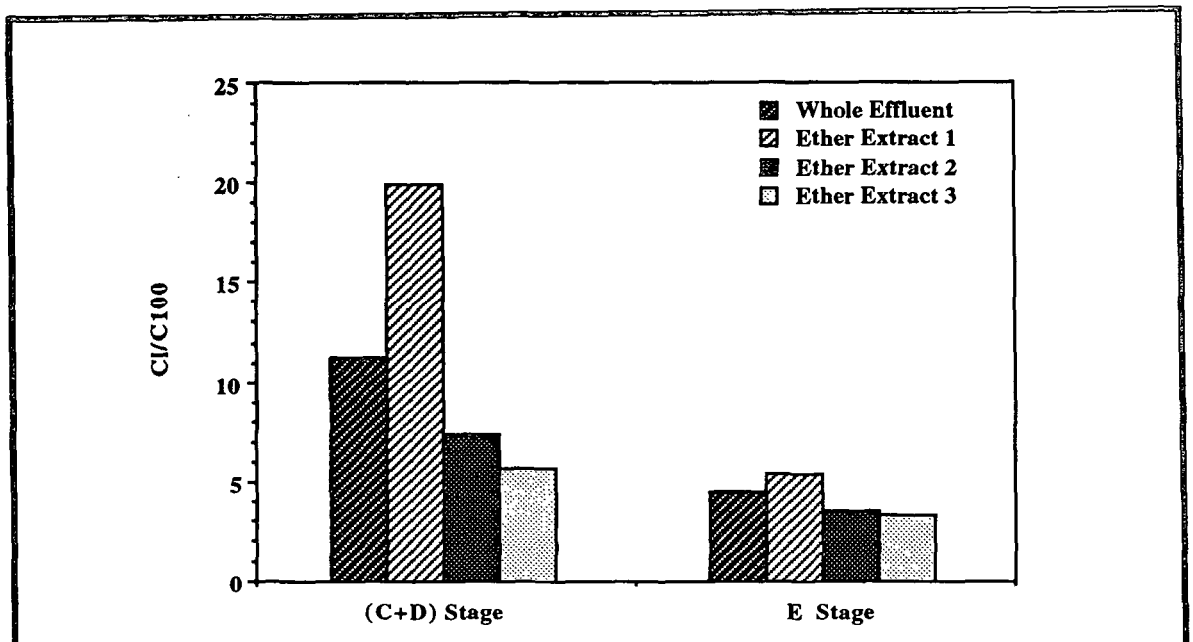

Figure 20. Cl/C_{100} Values for Ether Extracts and Whole Mill Produced Effluents.

Since the Cl/C_{100} of the first extract differed from that of the other extracts, and since the second and third extracts had essentially the same Cl/C_{100}, only 2 ether phases were collected in subsequent work. Extraction was done for 4 days, then the ether replaced and the extraction was continued for a total time of 14 days. The different chemical composition of the two ether phases and differences in polarity are likely to cause them to behave differently in the environment. For example, the second of 2 consecutive ether extracts was shown to exhibit decreased toxicity compared to the first.[126]

To ensure that carbon and chlorine were detectable in the relatively small phenolic and neutral subfractions of the ether extract, the extractor size was increased to 4 L. The 4 L extractors were subsequently used in the extractions of all laboratory produced effluents and in all model studies in this thesis.

When laboratory produced OC(EO) effluents were extracted using the 4 L extractors, Cl/C_{100} results for the 2 ether phases were comparable to the previous results for the mill produced chlorination effluents, as shown in Figure 21. The trends in the data were also the same. For example, the first ether phase (NVEE I) had a higher Cl/C_{100} than the whole effluents and the second ether phase (NVEE II) had a lower Cl/C_{100} than the whole effluents.

Model Extraction Studies

To demonstrate the validity of the ether extraction and effluent fractionation scheme, a series of model extraction systems were considered. De-ionized water and solutions of chloroacetic acid, 2,4,6-trichlorophenol, and p-bromophenol were all used as model extraction systems.

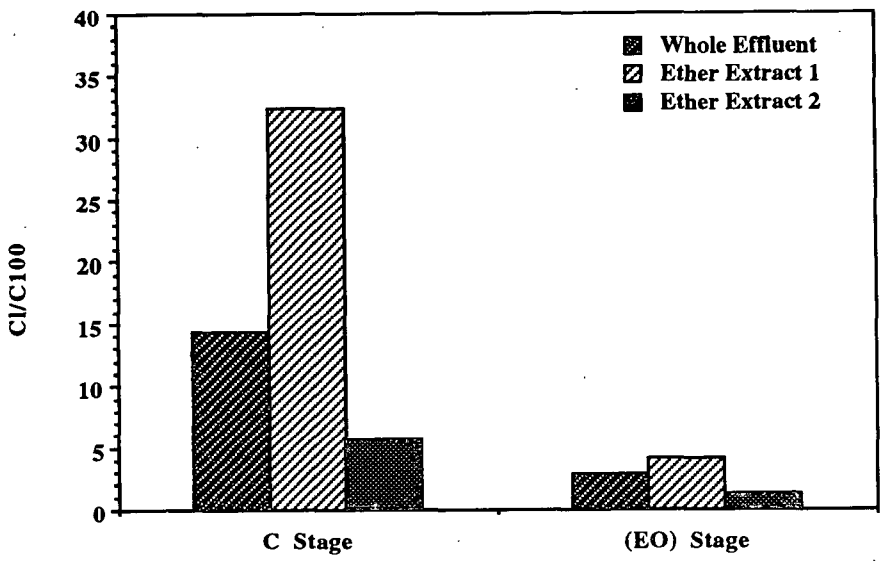

Figure 21. Cl/C_{100} Values for Ether Extracts and Whole Lab Produced OC(EO) Effluents.

De-ionized Water. De-ionized water was tested as a method blank for the extraction system. The purpose of the model system was to determine if ether alone, or in combination with any species in the water, resulted in a measurable level of TOC in any fraction. The largest amount of carbon was detected in the neutral subfraction of the ether extract, but was only 0.0445 mg TOC. This was only about 1% of the TOC found in the neutral fractions obtained from bleaching effluents, and was therefore of little significance.

Chloroacetic Acid. A solution of chloroacetic acid, containing about 188 ppb of organic chlorine, was prepared and continuously extracted. Only about 12 ppb AOX was measured on the original sample solution before extraction, and only about 8 ppb measured after evaporation of this sample. Therefore, only 6% of the total organic chlorine in the

original sample was determined by the AOX method, and another 33% of the detected material was lost upon evaporation. No chloroacetic acid was detected by the AOX method in any ether extract or extract subfractions. This shows that the AOX method is not an effective method for the determination of organic chlorine in highly polar, highly water soluble compounds such as chloroacetic acid, which probably do not adsorb to the carbon and cannot be detected. In addition to chloroacetic acid,[130] other compounds which have low AOX recoveries include chloroacetone,[130] and chloroethanol, benzylidenechloride, and trichlorotrifluoroethane.[168]

2,4,6-Trichlorophenol. A 2,4,6-trichlorophenol solution, containing about 272 ppb of organic chlorine, was prepared and extracted. The measured AOX level of the original sample before extraction was 254 ppb, but no AOX was detected in this sample after evaporation. However, this sample was about 10-400 times less concentrated in AOX than actual effluents and ether extracts. The entire loss of 254 ppb would represent a small fractional loss of the total AOX in an actual sample.

Since the entire amount of AOX was lost during evaporation, the fractions were not evaporated, and the Cl/C_{100} was not determined. AOX was still determined for each non-evaporated fraction. About 98% of the AOX was present in the phenolic fraction. Another 0.3% of the AOX was present in the acidic fraction, and the remainder was undetected.

p-Bromophenol. A solution of p-bromophenol, containing about 13.01 ppm AOX and 26.4 ppm TOC, was prepared and extracted. The p-bromophenol was chosen because of its solubility in both water and ether. A large enough quantity of p-bromophenol was dissolved in water so that once extracted into ether, the amounts of AOX and TOC within

the extract were on the same order of magnitude as those in the actual effluent extracts. The measured levels of AOX and TOC were 13.38 ppm and 25.0 ppm, resulting in a measured ratio of bromine to carbon (Br/C_{100}) of 17.9. The expected value is 16.8. About a 40% loss of both TOC and AOX occurred upon evaporation of the sample.

The p-bromophenol solution was subjected to the effluent fractionation scheme, and the results are given in Table VII. The Br/C_{100} value was close to the expected value for all fractions where p-bromophenol is likely to exist (NVEE I, NVEEP, Volatiles). The ratio was also near the expected value in the acid fraction, although it contained only 0.4% of the TOC. A relatively large amount of TOC existed within the neutral fraction and the Br/C_{100} value was 12.0, indicating less bromine than expected in p-bromophenol. However, analysis by GC/MS identified the major component of this fraction as p-bromophenol. The less than expected amount of bromine was possibly due to non-halogenated materials within this fraction.

Table VII. Extract Fractionation Results for p-Bromophenol Model Extraction Study.

Fraction	Br/C_{100}	% of Total TOC
Whole	17.9	108
NVW	17.5	64.3
NVEE I	17.5	68.0
NVEE II	333	0.00
NVNEE	333	0.00
NVEEA	16.1	0.36
NVEEP	18.9	46.9
NVEEN	12.0	8.72
Volatiles	18.9	44.0

Mass balances around the overall fractionation scheme (NVEE I + NVEE II + NVNEE + Volatiles) showed greater than 100% recovery of TOC and AOX. Similar balances around the ether extract fractionation (NVEEA + NVEEP + NVEEN) showed only 82-83% recovery of AOX and TOC.

Phenolic Recovery. Although some of the phenolic material was lost during sample evaporation, more phenolic material was recovered in this research than in previous studies. Comparative data are given in Table VIII. In this table, values for phenolic TOC and AOX were calculated from literature data. If only a sum of total phenolics was given, conservative assumptions about the percentages of organic carbon and organic chlorine were made. For TOC estimation, dichlorophenol was assumed to be the average phenol since it contains the highest percentage by weight of carbon among phenolics commonly found in bleaching effluents. Similarly, trichlorophenol was assumed as the average phenol for AOX estimation, since it contains the highest percentage by weight of chlorine. The validity of these assumptions is supported by the similarity of the actual and calculated Cl/C_{100} values.

Even using these conservative TOC and AOX estimates, more phenolic material was determined in this thesis (referenced as 169). Although it is possible that the phenolic fraction in this research was larger in size because it contained some acidic and neutral compounds, this is unlikely since fractionation was carried out by 3 successive extractions with the alkaline solutions. In most of the other studies the pulp had initial kappa numbers about twice as high, so more phenolics would be expected there. Since the kappa factor used in this research was higher than that normally used for chlorine bleaching and was probably higher than in other research, it could be argued that the increased level of phenolic material was a result. But a higher kappa factor should cause a higher

Table VIII. Summary of Phenolic Data.

Sequence	Initial Kappa	Phenolic TOC (g/t)	Phenolic AOX (g/t)	Cl/C_{100}	C/Cl	Reference
C_{80}DE	30.2	27*	33**	41	2.4	6
C_{80}DE	25.7	22*	27**	41	2.4	6
CE	30	36	46	43	2.3	39
C_{90}DE	26.4	23	26	38	2.6	96
CE	37	101*	124**	42	2.4	102
OC(EO)	14.1	196	116	20	5.0	169***
OC(EO)	14.1	196	96	17	6.0	169***

*TOC calculated assuming 44% carbon by weight - based on dichlorophenol as average phenol.

**AOX calculated assuming 54% chlorine by weight - based on trichlorophenol as average phenol.

***Present research

phenolic Cl/C_{100}, since an increased kappa factor increases the concentration of highly chlorinated phenolics.[26, 27] In the present study the Cl/C_{100} was actually lower than in previous work. This lower Cl/C_{100} was not likely to be due to losses of highly chlorinated phenolics, since highly chlorinated phenolics are generally less volatile than those with fewer chlorine substituents. For example, the Henry's law constant for chlorinated phenols and benzenes decreases as up to 3 chlorine substituents are added to the ring structures, and remains relatively constant when more than 3 chlorine substituents are present.[85]

Complex carbon rich and chlorine deficient phenolic fragments that are detected by the analysis methods of this research but not by the gas chromatography-based analyses done previously by others, could cause this observed decrease in the Cl/C_{100}. In most phenolic studies, gas chromatography (GC) was used to identify the compounds and only major peaks were identified. Noisy, unresolved, and overlapping peaks near the baseline were usually not identified, even though they represented a significant portion of the total chromatogram.[101, 104]

Extractor to Extractor Variation

To ensure that variation due to the use of two different 4 L ether extractors did not enter into the effluent fractionation and characterization data, each extractor was used once for each effluent type. Any extractor to extractor variation did not bias the results, since it entered into the experimental error term.

Since the extractors were systematically varied from effluent to effluent, a determination of the significance of extractor to extractor variation was set up. The existence of an extractor to extractor effect could be important information for future work in this area. A 3-way analysis of variance was done, where the three factors were bleaching se-

quence, bleaching stage, and extractor. Each bleaching condition was repeated, but there was no replication of extractions since each of the 2 extractors was used only once for each effluent type. The 3 factor interaction term was therefore used as the error estimate. Although this is not a perfect analysis, it is the best that can be done with the available data.

The analysis indicated that the extractor had a significant effect on the amount of TOC extracted in the first ether phase (NVEE I), but did not have a significant effect on the amount of TOC extracted in the second ether phase (NVEE II) or on overall extracted TOC. Extraction rate was greatest early in the extraction, so any differences in extraction rate would be expected to be most clearly observed in the NVEE I fraction.

Section 2 Conclusions

These results were important to the development of the ether extraction based effluent fractionation scheme and in validation of the fractionation methods. They also indicated how certain variables affected the fractionation process.

Material extracted by ether, from effluents, during an initial short extraction period, was much more concentrated in organic chlorine than either the whole effluent itself or the material extracted at longer times. The fractionation scheme, including 2 distinct ether extract fractions, was developed as a result of the strong dependence of ether extract organochlorine concentration on extraction time.

No significant quantity of TOC was detected in any effluent fraction when deionized water was extracted with ether. Highly polar model compounds were poorly extracted by ether, and poorly detected by the AOX method. Phenolic compounds partitioned predominantly into the phenolic fraction, but some phenolic material was lost during sample evaporation. However, far more phenolic material was recovered in this research than in previous research.

Different ether extractors removed different amounts of material from effluents during the immediate short extraction interval, but removed similar amounts of material during a second consecutive, longer term extraction period. The overall level of removed material (total of both extraction periods) did not differ.

Section 3: Characterization of Effluent Fractions from ClO_2 and Cl_2 Bleaching of Unbleached and O_2 Bleached Softwood Kraft Pulps

The effluents from ECF bleaching sequences and conventional chlorine bleaching (the OC(EO), OD(EO), and D(EO) sequences) were compared in Section 3, using the ether extraction based fractionation procedure.

The use of 100% ClO_2 to replace chlorine may be more environmentally beneficial than suggested by the decreased levels of AOX. Environmentally significant effluent fractions, including the ether soluble, phenolic, and neutral fractions all had decreased ratios of chlorine to carbon, when ClO_2 replaced chlorine. In addition, the proportion of material within the ether soluble and phenolic fractions decreased significantly when ClO_2 was used.

The use of O_2 delignification before 100% ClO_2 bleaching had similar benefits. In addition to producing only half the effluent load, oxygen delignification decreased the ratio of chlorine to carbon in the environmentally significant phenolic and neutral fractions.

CHARACTERIZATION OF EFFLUENT FRACTIONS FROM ClO_2 AND Cl_2 BLEACHING OF UNBLEACHED AND O_2 BLEACHED SOFTWOOD KRAFT PULPS

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ABSTRACT

Effluents from OC(EO), OD(EO), and D(EO) laboratory bleaching of softwood kraft pulp were characterized by fractionation and analysis of the fractions. The fractionation consisted of ether extraction followed by separation of the extract into acidic, phenolic, and neutral subfractions. Each fraction was characterized in terms of its size, and in terms of its ratio of chlorine to carbon.

Replacement of chlorine with chlorine dioxide after oxygen bleaching sharply reduced the adsorbable organic halide (AOX), total organic carbon (TOC), and chlorine to carbon ratio (expressed as the number of chlorine atoms per 100 carbon atoms, Cl/C_{100}) of the whole effluents. Larger AOX, TOC, and Cl/C_{100} reductions were seen in the ether soluble fraction and in the phenolic subfraction of the ether soluble material. Replacement of chlorine by chlorine dioxide may therefore be more beneficial than the resulting reductions in whole effluent AOX suggest.

Oxygen delignification prior to a 100% chlorine dioxide stage reduced whole effluent AOX and TOC in rough proportion to the amount of lignin removed in the oxygen stage, but did not affect the overall Cl/C_{100}. There was a significant reduction in the Cl/C_{100} of both the phenolic and neutral subfractions of the ether extract. Oxygen delignification, like chlorine dioxide substitution, may therefore be more beneficial than the overall AOX reduction suggests.

INTRODUCTION

Proposed regulation of adsorbable organic halide (AOX) and the consumer's desire to buy "environmentally friendly" products, has led pulp mills to implement AOX reduction strategies. The level of AOX in pulp bleaching effluents can be decreased by the following process changes: improved brownstock washing, extended delignification, O_2 delignification, substitution of chlorine dioxide for chlorine, and oxidative caustic extraction.

Although process changes can reduce AOX, the effect on the environment remains uncertain (1, 2). Since only a small fraction of the AOX is potentially harmful, reducing the overall level of AOX may or may not reduce an effluent's environmental effects. Hundreds or perhaps thousands of compounds, including certain environmentally troublesome ones, have been identified within the small fraction of the effluent that is considered potentially harmful. These include chlorophenolics (3-11), chlorinated dioxins (3, 8, 12), chlorinated neutral compounds (11, 13, 14), chlorinated carboxylic acids (11, 15) and chloroform (6, 16).

The complexity of pulp bleaching effluents complicates the task of developing bleaching processes that eliminate the potential for harmful effects on the environment. Ideally, a full chemical characterization could be done on effluents from a variety of process alternatives, and data on the environmental effects of each component would be available. It would then be simple to choose the process that results in minimum environmental effect. Effluents are sufficiently complex to defy full chemical characterization, however. For example, the toxicity of effluents can only be partially accounted for by identified components (7).

A practical alternative to the impossible ideal of complete analysis is fractionation of the effluents and characterization of the fractions in terms that will allow prediction of environmental effects. Such an approach was adopted in the present study. Fractionation was conducted on the basis of ether solubility, volatility and acidity, and the fractions were characterized in terms of their relative size and chlorine to carbon ratios. Ether solubility implies low molecular weight (17, 18), and low molecular weight material may be correlated with acute and chronic toxicity (2, 19). The ether extract contains most of the effluent's mutagenicity (13, 20, 21) and toxicity (17), and the chlorine to carbon ratio may be used as a predictor of toxicity (7,

22, 23) and lipophilicity (24) within certain classes of compounds.

EXPERIMENTAL APPROACH

Pulp Bleaching

Three different pulp bleaching sequences were considered in this work: OC(EO), OD(EO), and D(EO). The unbleached pulp was a mill produced kraft with a kappa number of 26.0. The oxygen bleached pulp (kappa 14.1) was collected after the oxygen stage at the same mill. Both pulps were well washed. Only the first two stages of pulp bleaching were done, since they produce most of the effluent load.

Effluent Fractionation and Characterization

For reasons mentioned above, effluent characterization was based on ether extraction. This type of procedure has been used in previous studies of mutagenicity (21, 25) and toxicity (17), and isolations and analyses of chlorophenols (9, 22), chlorinated neutral compounds (14, 26), and chlorinated carboxylic acids (15).

Figure 1 depicts the effluent fractionation scheme, and Table I lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted exhaustively with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions: a non-extractable fraction, and two ether extractable fractions. The first ether fraction (the least polar of the two ether fractions) is readily extracted and the second, more polar fraction, is removed slowly over an extended period. The first ether extract was further fractionated into acids, phenolics, and neutrals.

The number of organically bound chlorine atoms per hundred carbon atoms (Cl/C_{100}), was determined for each effluent and effluent fraction. To measure Cl/C_{100} on the ether extract and extract fractions, the ether was first completely removed, then AOX and total organic carbon (TOC) measured on each fraction. To remove the ether each fraction was evaporated, as represented in Figure 1 by the dashed horizontal lines, to yield the final samples. Information on the volatile effluent components removed during evaporation was obtained by evaporation of whole effluent samples and comparison of the remaining "non-volatile" TOC and AOX with the TOC and AOX of the whole effluent.

Data Analysis

All bleaching sequences were performed in duplicate, and effluents from the individual stages for each replication were fractionated and analyzed separately. This resulted in two completely independent sets of data for each sequence. Analyses of variance (AOV) were done on the data from each fraction, to assess the significance of differences between sequences and between stages. Since data with high Cl/C_{100} clearly had a greater variance than the low Cl/C_{100} data, all Cl/C_{100} data were log transformed to stabilize variance. When AOV showed a significant effect between bleaching sequences, least significant differences were determined using Duncan's multiple range test (27).

RESULTS AND DISCUSSION

In this report only the whole effluents, the ether soluble fraction, the phenolics, and the neutrals are considered, since evidence in the literature suggests that these fractions are more environmentally important than the others. The other fractions are discussed elsewhere (28). The Cl/C_{100} and the percentage of total TOC are emphasized. The Cl/C_{100} is a predictor of the relative environmental behavior of the material, and the percentage of the total TOC gives a measure of the total amount of material. The percentage of total TOC is used in order to normalize the TOC data for different levels of delignification.

All TOC, AOX, and Cl/C_{100} data are presented in Tables II-V for the whole effluents and the fractions. The total TOC and AOX (given in Table II) represents TOC and AOX mass balances around the fractionation scheme and were determined as the sums of the AOX and TOC determinations of the neutrals, the phenolics, the acids, the polar fraction, the hydrophilic fraction, and the volatiles.

The data are presented as bar graphs which consist of 3 groups of bars. Each group consists of 3 bars, representing the OD(EO), OC(EO), and D(EO) bleaching sequences respectively. The first group, labeled D/C, refers to the effluents produced in the 100% D or 100% C delignification stages. The second group, labeled (EO), refers to oxidative caustic extraction stage effluents. The final group, labeled D/C + (EO), presents the summed data from the first and second stages of

bleaching. Combined first and second stage effluents were not tested. The summed data are presented only as rough estimates of the combined effluent properties.

Whole Effluents

Kappa numbers after the (EO) stage were 1.9, 4.3, and 5.1 respectively, for the OC(EO), OD(EO), and D(EO) sequences. Figure 2 compares the three bleaching sequences with respect to mean TOC production, which provides a measure of the total organic load produced by each sequence. As expected, based on the higher pulp kappa number entering the sequence, the D(EO) sequence produces the greatest quantity of TOC. In the case of the oxygen based sequences, about half of the organic material has already been removed in the oxygen stage prior to delignification with chlorine based chemicals. This material is recycled to the mill's recovery system and is therefore without environmental significance in the wastewater stream.

A comparison of the oxygen based sequences shows that chlorine produces more TOC than chlorine dioxide in both the D/C and (EO) stages. This is in part due to the more effective delignification done by chlorine, but the difference is too great to be due to this effect alone. The data suggest that the OD(EO) sequence gives a higher carbohydrate yield (28).

Figure 3 presents a similar comparison of mean Cl/C_{100}. In both stages the material released by chlorine bleaching is much more extensively chlorinated than that released by chlorine dioxide bleaching. This is expected since chlorine reacts by both oxidation and substitution while chlorine dioxide only reacts by oxidation. The ClO_2 bleaching produces some chlorinated organics as well, as a result of the formation and reaction of HOCl and Cl_2 during the process.

Insertion of an O_2 stage before ClO_2 has little effect on the extent of chlorination of effluent compounds, although some decrease is seen in the case of the (EO) stage effluents. This may be a result of the action of O_2 delignification. Oxygen in alkaline solution oxidizes free phenolic structures, thus reducing the number of sites that are readily substituted by chlorine. Another possible explanation is that material from the OD(EO) sequence is more readily de-chlorinated in the caustic extraction stage than material from the D(EO) sequence.

Ether Soluble Fraction

A change from chlorine to chlorine dioxide bleaching reduces TOC, AOX, and the Cl/C_{100} in the ether soluble fraction to a greater extent than occurs in the whole effluent.

Figure 4 presents the mean ether soluble TOC as a percentage of total TOC for each bleaching sequence. For both the D/C and (EO) stages, chlorine use results in a higher ether soluble TOC content than chlorine dioxide use. The D(EO) sequence has a smaller percentage of total TOC in this fraction than OD(EO). Because of the increased lignin removal however, the absolute amounts of AOX and TOC in this fraction are greater for the D(EO) sequence.

Figure 5 similarly compares the sequences with regard to Cl/C_{100}. For both the D/C and (EO) stages, this fraction contains increased chlorine per unit carbon compared to the whole effluents. This further supports the contention that the ether soluble fraction is of environmental interest. The ether soluble fraction is also chlorinated to a much greater extent when chlorine is used rather than chlorine dioxide. The increased degree of chlorine substitution on the organic material in the case of chlorine results in a more nonpolar effluent and is a possible cause of the increased proportion of ether soluble TOC. Use of chlorine dioxide provides two environmental benefits over chlorine use, in the case of the ether soluble material: a large reduction in the amount of organically bound chlorine per unit carbon, and a reduced amount of material within the fraction. There is no significant Cl/C_{100} effect observed between the OD(EO) and D(EO) sequences.

Phenolic Fraction

When the change is made from chlorine to chlorine dioxide bleaching, TOC, AOX, and the Cl/C_{100} are reduced to a greater extent in this fraction than in the whole effluent. This parallels the effect on the ether soluble fraction.

Figure 6 compares the phenolic TOC as a percentage of total TOC for the three sequences. Chlorine bleaching results in an increased proportion of phenolic TOC relative to chlorine dioxide for both the D/C and (EO) stages. The reduced amount of phenolic material with ClO_2 bleaching is in accordance with other studies in which the amount of measured chlorophenolics decreased as ClO_2 substitution increased (5, 7, 11).

Figure 7 compares the phenolic fraction Cl/C_{100} for the three bleaching sequences and for both stages. Chlorine produces a much more extensively chlorinated phenolic fraction than does chlorine dioxide. The two benefits from the use of chlorine dioxide rather than chlorine are again seen here: decreased phenolic AOX per unit carbon, and a decreased amount of material in the phenolic fraction.

No significant differences were seen between the OD(EO) and D(EO) sequences by the normal AOV. However if only the OD(EO) and D(EO) data were included in the analysis, a significantly greater Cl/C_{100} is seen for D(EO) bleaching compared to OD(EO).

Neutral Fraction

Figure 8 compares the bleaching sequences with regard to neutral fraction TOC expressed as a percentage of the total TOC. There are no statistically significant differences between any of the bleaching sequences, due to scatter in the replicate data.

Figure 9 compares the neutral fraction Cl/C_{100} for the sequences. Again chlorine produces a more highly chlorinated material than does chlorine dioxide, for both D/C and (EO) stages. The D(EO) sequence also produces a more highly chlorinated material than the OD(EO) sequence. This is another indication that oxygen delignification leaves a residual lignin that is less susceptible to chlorine substitution reactions than unoxidized lignin.

EXPERIMENTAL METHODS

The experimental methods regarding pulp bleaching, ether extraction of effluents, and ether extract fractionation are considered here. Details on effluent and sample preparation, TOC analysis, and AOX analysis are provided elsewhere (28).

D/C Stage Pulp Bleaching

All D/C stages were done in a 20 L batch reactor, designed to rapidly add bleaching chemicals. Bleaching was done at 2% consistency, at 45°C, for 30 minutes, and at a kappa factor of 0.25. The mixer was run at 350 rpm. Initial pH in all cases was adjusted to 2 by the addition of sulfuric acid solution.

(EO) Stage Pulp Bleaching

All (EO) stages were done in a Quantum Technologies high shear mixer at 10% consistency, at 70°C, and for 70 minutes. The NaOH charge was 0.55 X TAC, the O_2 charge was 0.5% on pulp, and 4.1% of the total D/C stage filtrate was included as carryover. The slurry was mixed at 15 Hertz for 3 seconds, every 5 minutes.

Ether Extraction of Effluents

Ether extraction was done on 4 L of effluent using continuous liquid-liquid extractors. Extraction was carried out with 500 ml of diethyl ether. The first ether phase was collected after 96 hours of extraction and was replaced with 500 ml of fresh ether. Extraction was continued for 336 total hours. The extraction was then stopped and the second ether phase and the non-extractable materials were collected.

Ether Extract Fractionation

The first ether phase was diluted to 500 ml, 100 ml of the sample collected, and the remaining ether placed in a separatory funnel for fractionation. The ether was extracted 3 times with 25 ml of 0.5 M $NaHCO_3$, and the extracts collected and acidified. The ether was next extracted 3 times with 25 ml of 0.5 M NaOH, and these extracts also collected and acidified. The $NaHCO_3$ soluble material is the acidic fraction, the NaOH soluble material is the phenolic fraction, and the remaining ether soluble material is the neutral fraction.

SUMMARY AND CONCLUSIONS

The D(EO) bleaching sequence produces about twice as much AOX and TOC as the OD(EO) sequence, as expected based on the higher kappa number of the unbleached pulp. The OC(EO) sequence produces more effluent TOC than OD(EO) because of increased delignification effectiveness of chlorine, and possibly also increased carbohydrate loss. The OC(EO) sequence also produces much more AOX than the OD(EO) sequence.

Certain significant conclusions regarding the nature of bleaching effluents produced by both chlorine and chlorine dioxide bleaching can be made, based on the results of this research. For the whole effluents, chlorine bleaching gives a higher Cl/C_{100} than ClO_2 bleaching of the same pulp. The same trend is seen for effluent fractions which are environmentally significant. In the case of the ether soluble fraction and the

phenolic fraction, not only is the Cl/C_{100} greater for Cl_2 bleaching, but a greater percentage of the total TOC partitions into the ether soluble and phenolic fractions as well. The phenolic and neutral fractions for both the D/C and (EO) stages have lower Cl/C_{100} values when oxygen bleaching precedes chlorine dioxide treatment.

The results of this research provide some new evidence in support of the use of chlorine dioxide and O_2 delignification as a means of environmental improvement. By using ClO_2 in place of Cl_2, not only is the amount of chlorine substitution on organic compounds greatly reduced, but the percentage of material within certain environmentally important fractions is also reduced. Oxygen bleaching, in addition to the expected benefit of reducing in half the total effluent load, provides a decreased level of chlorine substitution on organic compounds in the phenolic and neutral fractions of both D/C and (EO) stage effluents. Therefore, both chlorine dioxide substitution and oxygen bleaching may be more environmentally beneficial than the overall AOX reduction suggests.

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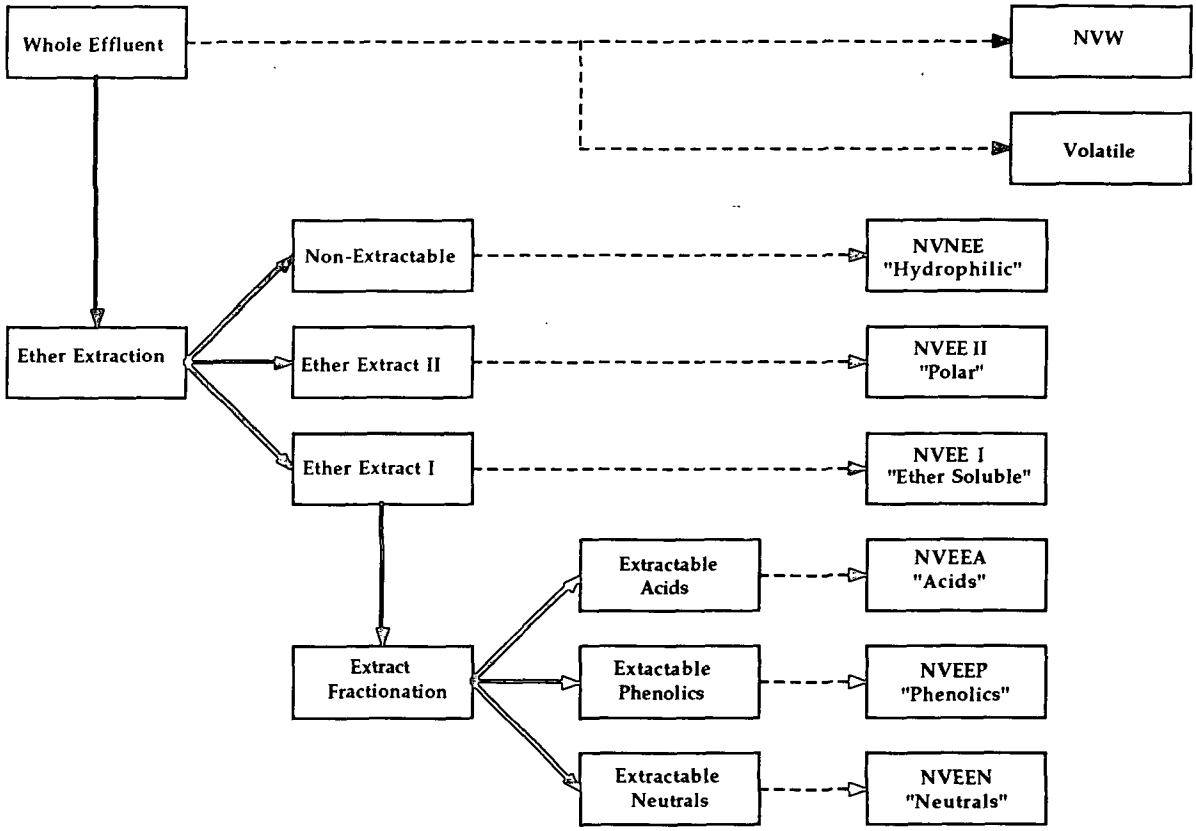
Figure 1. Effluent Fractionation.



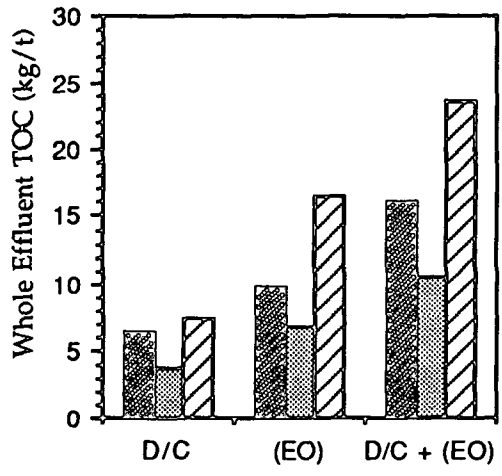


Figure 2. Whole Effluent TOC.

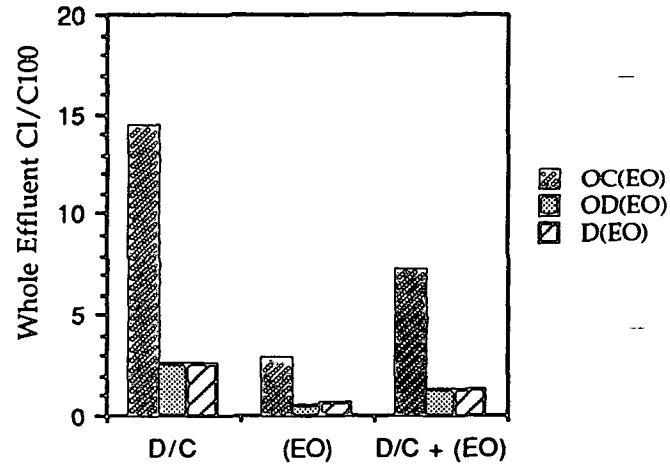


Figure 3. Whole Effluent Cl/C100.

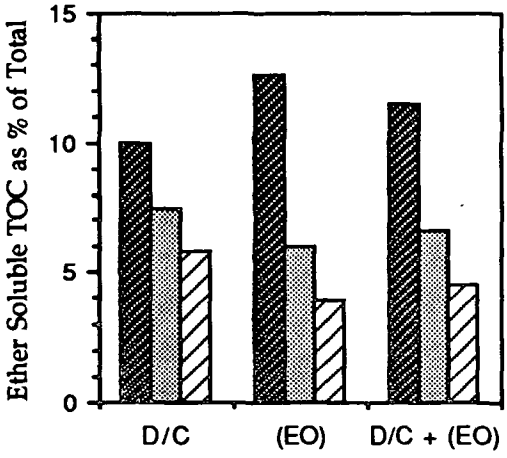


Figure 4. Ether Soluble TOC as % of Total.

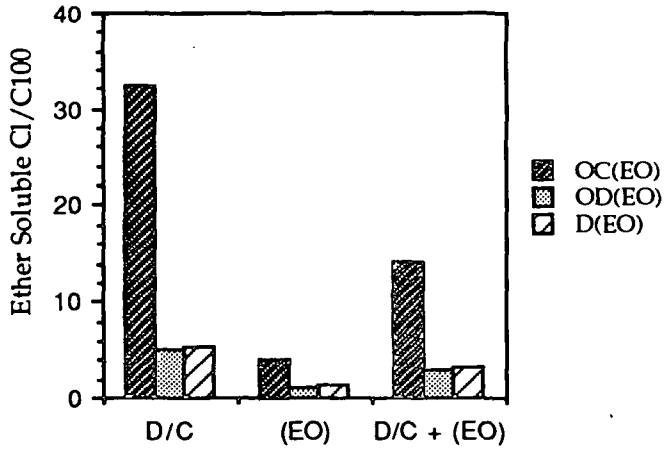


Figure 5. Ether Soluble Cl/C100.

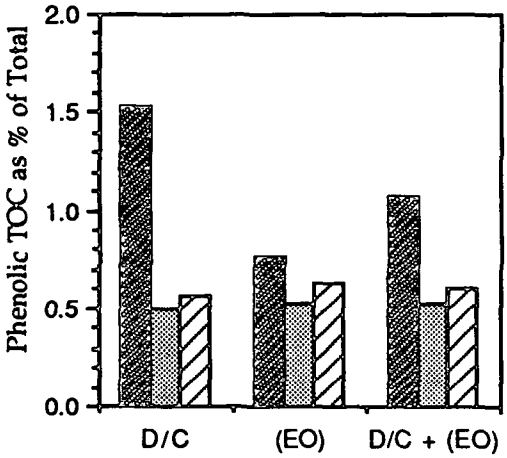


Figure 6. Phenolic TOC as % of Total.

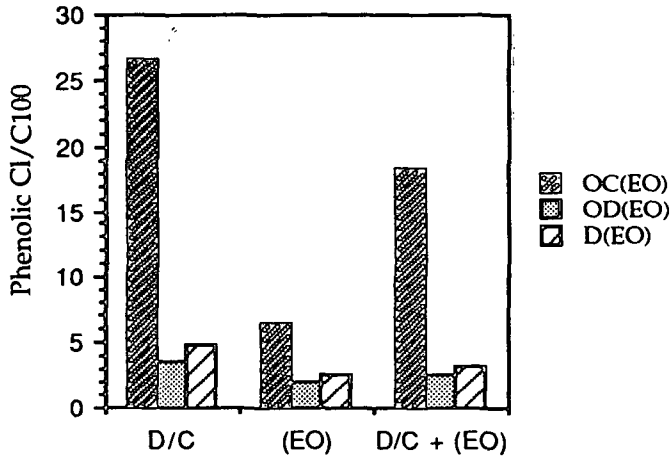


Figure 7. Phenolic Cl/C100.

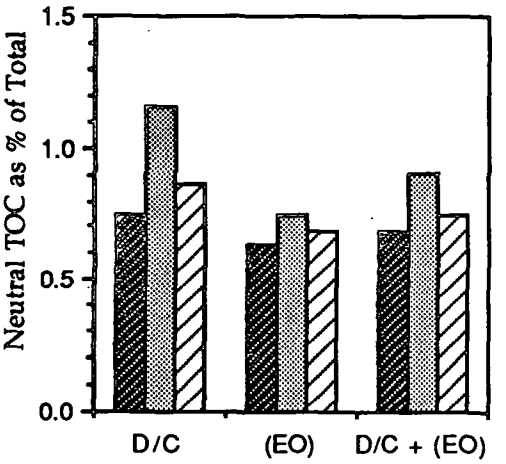


Figure 8. Neutral TOC as % of Total.

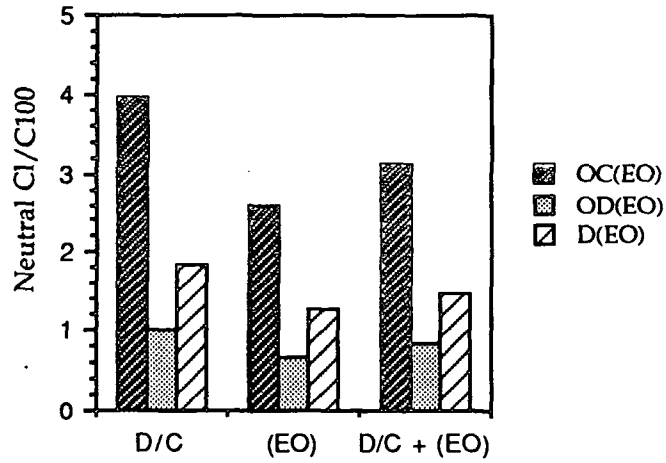


Figure 9. Neutral Cl/C100.

Table I. Effluent Fraction Codes and Descriptions of Fractions.

Fraction Code	Description
NVW	Non-volatile, whole effluent.
NVNEE	Non-volatile, not extracted with ether ("Hydrophilic").
NVEE II	Non-volatile, difficult to extract with ether ("Polar").
NVEE I	Non-volatile, readily ether extractable ("Ether Soluble").
NVEEA	Non-volatile, ether extractable acidic compounds ("Acids").
NVEEP	Non-volatile, ether extractable phenolic compounds ("Phenolics").
NVEEN	Non-volatile, ether extractable neutral compounds ("Neutrals").

Table II. Whole Effluent and Summed Fraction Characteristics.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	6.15	6.36	3.85	3.80	7.33	7.23
Total TOC[a], kg/t	7.03	8.17	4.43	4.29	7.87	8.02
AOX, kg/t	2.75	2.56	0.299	0.294	0.552	0.594
Total AOX[a], kg/t	2.26	2.13	0.297	0.264	0.447	0.551
Cl/C_{100}	15.1	13.6	2.63	2.61	2.54	2.78
(EO) Stage						
TOC, kg/t	9.37	10.2	6.79	6.60	17.1	15.7
Total TOC[a], kg/t	9.83	11.6	6.70	6.52	15.6	14.9
AOX, kg/t	0.793	0.858	0.101	0.102	0.341	0.309
Total AOX[a], kg/t	0.738	0.887	0.0938	0.0930	0.324	0.306
Cl/C_{100}	2.86	2.86	0.50	0.52	0.68	0.67
D/C + (EO) Stage						
TOC, kg/t	15.5	16.6	10.6	10.4	24.4	22.9
Total TOC[a], kg/t	16.9	19.8	11.1	10.8	23.5	22.9
AOX, kg/t	3.54	3.42	0.400	0.396	0.893	0.903
Total AOX[a], kg/t	3.00	3.02	0.391	0.357	0.771	0.857
Cl/C_{100}	7.71	6.98	1.27	1.29	1.24	1.33

[a]Sum of corresponding values for volatile, hydrophilic, polar, acid, phenolic, and neutral fractions.

Table III. Ether Soluble Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.681	0.832	0.383	0.267	0.501	0.418
% of Total TOC	9.69	10.2	8.65	6.22	6.37	5.21
AOX, kg/t	0.790	0.632	0.0547	0.0439	0.0751	0.0725
% of Total AOX	35.0	29.7	18.4	16.6	16.8	13.2
Cl/C_{100}	39.2	25.6	4.83	5.56	5.05	5.88
(EO) Stage						
TOC, kg/t	1.32	1.36	0.406	0.399	0.663	0.542
% of Total TOC	13.4	11.7	6.06	6.12	4.25	3.64
AOX, kg/t	0.173	0.154	0.0127	0.0125	0.0273	0.0220
% of Total AOX	23.4	17.4	13.5	13.4	8.43	7.19
Cl/C_{100}	4.44	3.83	1.06	1.06	1.39	1.37
D/C + (EO) Stage						
TOC, kg/t	2.00	2.19	0.789	0.666	1.16	0.960
% of Total TOC	11.9	11.1	7.09	6.16	4.94	4.19
AOX, kg/t	0.963	0.786	0.0674	0.0564	0.102	0.0945
% of Total AOX	32.1	26.0	17.2	15.8	13.2	11.0
Cl/C_{100}	16.3	12.1	2.89	2.86	2.97	3.33

Table IV. Phenolic Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.108	0.123	0.0239	0.0198	0.0462	0.0434
% of Total TOC	1.54	1.51	0.54	0.46	0.59	0.54
AOX, kg/t	0.0935	0.0869	0.00255	0.00201	0.00683	0.00602
% of Total AOX	4.14	4.08	0.86	0.76	1.53	1.09
Cl/C_{100}	29.2	23.8	3.60	3.45	5.00	4.69
(EO) Stage						
TOC, kg/t	0.0884	0.0725	0.0364	0.0341	0.0820	0.107
% of Total TOC	0.90	0.63	0.54	0.52	0.53	0.72
AOX, kg/t	0.0221	0.00924	0.00243	0.00180	0.00697	0.00730
% of Total AOX	2.99	1.04	2.59	1.94	2.15	2.39
Cl/C_{100}	8.47	4.31	2.26	1.79	2.87	2.31
D/C + (EO) Stage						
TOC, kg/t	0.196	0.196	0.0603	0.0539	0.128	0.150
% of Total TOC	1.16	0.99	0.54	0.50	0.55	0.65
AOX, kg/t	0.116	0.0961	0.00498	0.00381	0.0138	0.0133
% of Total AOX	3.87	3.18	1.27	1.07	1.79	1.55
Cl/C_{100}	20.0	16.6	2.79	2.39	3.64	3.00

Table V. Neutral Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.0393	0.0750	0.0551	0.0457	0.0784	0.0583
% of Total TOC	0.56	0.92	1.24	1.07	1.00	0.73
AOX, kg/t	0.00591	0.00629	0.00153	0.00148	0.00342	0.00387
% of Total AOX	0.26	0.30	0.52	0.56	0.77	0.70
Cl/C_{100}	5.08	2.83	0.94	1.09	1.48	2.24
(EO) Stage						
TOC, kg/t	0.0671	0.0676	0.0511	0.0480	0.0685	0.137
% of Total TOC	0.68	0.58	0.76	0.74	0.44	0.92
AOX, kg/t	0.00520	0.00513	0.00129	0.000701	0.00275	0.00495
% of Total AOX	0.71	0.58	1.38	0.75	0.85	1.62
Cl/C_{100}	2.62	2.56	0.85	0.49	1.36	1.22
D/C + (EO) Stage						
TOC, kg/t	0.106	0.143	0.106	0.0937	0.147	0.195
% of Total TOC	0.63	0.72	0.95	0.87	0.63	0.85
AOX, kg/t	0.0111	0.0114	0.00282	0.00218	0.00617	0.00882
% of Total AOX	0.37	0.38	0.72	0.61	0.80	1.03
Cl/C_{100}	3.54	2.69	0.90	0.79	1.42	1.53

Section 3 Conclusions

Effluents from low AOX bleaching sequences [OD(EO), D(EO)] were compared to those from conventional chlorine bleaching [OC(EO)], using the ether extraction based fractionation scheme.

The use of 100% ClO_2 to replace chlorine may be more environmentally beneficial than suggested by the decreased levels of AOX. Environmentally significant effluent fractions, including the ether soluble, phenolic, and neutral fractions all had decreased ratios of chlorine to carbon, when ClO_2 replaced chlorine. In addition, the proportion of material within the ether soluble and phenolic fractions decreased significantly when ClO_2 was used.

The use of O_2 delignification before 100% ClO_2 bleaching had similar benefits. In addition to producing only half the effluent load, oxygen delignification decreased the ratio of chlorine to carbon in the environmentally significant phenolic and neutral fractions.

Section 4: The Effect of D Stage pH on Effluent Quality: Characterization of Effluent Fractions from OD(EO) Bleaching of Softwood Kraft Pulp

In Section 4 effluents from the OD(EO) bleaching sequence with the D stage begun at two different pH levels were compared. The ether extraction based fractionation was the basis for the effluent characterization.

Based on the composition of environmentally significant effluent fractions, neither initial D stage pH level appeared to represent an advantage from an environmental point of view. The OD(EO) sequence with the D stage begun at pH 2, produced a smaller proportion of material within the environmentally significant ether soluble and phenolic fractions than the sequence with the D stage begun at pH 4. However, at pH 2 the ether soluble and phenolic material was substituted to an increased extent by chlorine atoms. The result was a similar quantity of ether soluble and phenolic AOX in both cases.

The D stage begun at pH 4 achieved greater delignification than the pH 2 case. To achieve the same delignification, less ClO_2 per unit of lignin must therefore be applied when the D stage is begun at pH 4, and all organic material will be substituted by fewer chlorine atoms. This could represent an environmental advantage in addition to cost savings associated with the decreased ClO_2 use.

THE EFFECT OF D STAGE PH ON EFFLUENT QUALITY: CHARACTERIZATION OF EFFLUENT FRACTIONS FROM OD(EO) BLEACHING OF SOFTWOOD KRAFT PULP

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ABSTRACT

Effluents from OD(EO) laboratory bleaching of softwood kraft pulp were characterized by fractionation and analysis of the fractions. The fractionation consisted of ether extraction followed by separation of the extract into acidic, phenolic, and neutral subfractions. The effluents from the sequence with the D stage begun at pH 2 (D-pH 2 bleaching) were compared to the same sequence with the D stage begun at pH 4 (D-pH 4 bleaching). Adsorbable organic halide (AOX) and total organic carbon (TOC) were determined for the whole D and (EO) effluents as well as for the fractions from both stages. Each fraction was characterized in terms of its ratio of chlorine to carbon (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}) and in terms of its size, expressed as a percentage of the total TOC generated. The Cl/C_{100} is a likely predictor of environmental effects.

D-pH 4 bleaching resulted in a reduced kappa number in the extracted pulp compared to the D-pH 2 case. This is consistent with the whole effluent TOC data, in which D-pH 4 bleaching produced more D stage TOC than D-pH 2. The (EO) stage TOC remained constant. D-pH 4 bleaching gave lower chlorine-to-carbon ratios in effluents from both the D and (EO) stages.

The ether extractable material and the phenolic fraction, both of which contain compounds of environmental interest, exhibited decreased Cl/C_{100} values for D-pH 4 bleaching. Since the percentage of total TOC within these fractions was higher, overall AOX levels were nearly equal. Because of the greater delignification at D-pH 4 conditions, environmental and economic benefits may be realized by a reduction of the applied ClO_2 charge.

INTRODUCTION

It is generally accepted that bleaching at a pH of 2 or less results in greater delignification effectiveness for chlorine bleaching (1), for mixtures of chlorine and chlorine dioxide (2), and for chlorine dioxide alone (2, 3, 4, 5). However within the pH range of 2 to 4, and particularly for O_2 delignified pulps, an initial pH above 2 may be more effective (2, 3, 6).

The pH of a chlorination stage also has an effect on the quality of the effluent produced in the stage. The rates of formation of both chlorinated dioxins (7, 8) and chlorinated phenolic compounds (9, 10) are reduced by increased C stage pH. Total AOX is reduced at increased pH for both chlorine and chlorine dioxide bleaching (2).

Pulp bleaching effluents in general have been characterized with respect to adsorbable organic halide (AOX) (11-15) and in terms of individual compounds or environmentally significant groups of compounds such as chlorophenolics (9, 10, 15-21), chlorinated dioxins (7, 8, 18), chlorinated neutral compounds (21-23), chlorinated carboxylic acids (21, 24), and chloroform (17, 25).

Because of the complexity of the effluents, these analyses give an incomplete picture of likely environmental effects. An alternative is analysis of the effluent by fractionation into meaningful classes of compounds, followed by relevant characterization of the fractions. One such procedure, based on ether extraction, has been developed and applied to effluents produced by D(EO), OD(EO), and OC(EO) sequences (26). Ether extraction was chosen as the basis for this procedure because virtually all effluent components known to be significant from an environmental point of view are found in the extracts. Chlorine-to-carbon ratios (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}), which may predict environmental behavior, were determined for the fractions. The same fractionation and characterization methods were used for the present study of the effects of D stage initial pH in OD(EO) bleaching of softwood kraft pulp.

EXPERIMENTAL APPROACH

Pulp Bleaching

A mill-produced, oxygen-bleached kraft pulp with a kappa number of 14.1 was bleached by an OD(EO) se-

quence in the laboratory. The pulp was well washed before bleaching. Only the first two stages of bleaching were done, since most of the delignification and most of the effluent load production occurs in these stages.

The D stages were done in a specially designed batch reactor, and the (EO) stages were done in a high shear mixer. For the D stages, the pH of the pulp slurry was adjusted to an initial level of 2 (D-pH 2 bleaching) or 4 (D-pH 4 bleaching) by the addition of sulfuric acid solution. In the D-pH 2 stage, the pH remained essentially constant throughout, while in the D-pH 4 stage it decreased to a final level of near 2.5. Kappa numbers after bleaching are given in Table I.

Effluent Fractionation and Characterization

The effluents produced in this study were fractionated by ether extraction, and the ether extractable material was further separated into acidic, phenolic, and neutral fractions. To measure Cl/C_{100} on the ether extract and its fractions, the ether was exhaustively removed by evaporation, and AOX and TOC were then measured on each fraction. During evaporation, volatiles other than ether were also removed. To obtain information on the volatile fraction, a sample of the whole effluent was similarly evaporated and the carbon and chlorine losses determined.

Figure 1 depicts the effluent fractionation scheme, and Table II lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions: a non-extractable fraction and two ether extractable fractions. The first ether fraction is material readily extracted, and the second is removed slowly over an extended period. The first was further fractionated into acids, phenolics, and neutrals. Each fraction was then evaporated, as represented in Figure 1 by the dashed horizontal lines, to yield the final samples.

Data Analysis

The D-pH 2 and D-pH 4 bleaching sequences were performed in duplicate, and the effluents from the D and (EO) stages of bleaching were fractionated and analyzed separately. This resulted in two completely independent sets of data for each sequence.

Analyses of variance (AOV) were done on the data from each fraction to assess the significance of differences between pH levels and between stages. Since data with high Cl/C_{100} had a greater variance than the low Cl/C_{100} data, all Cl/C_{100} data were log transformed to stabilize variance. When AOV showed a significant effect between pH levels, a least significant difference was determined using Duncan's multiple range test (27).

RESULTS AND DISCUSSION

Data for the whole effluents and for the ether soluble and phenolic fractions are given in Tables III-V. These fractions are considered here because significant pH effects are observed within them. The delignification of the pulp and its implications are also considered here. The other fractions are considered elsewhere (28).

The total TOC and AOX (given in Table III) represent TOC and AOX mass balances around the fractionation scheme. Total AOX and TOC were determined as the sums of the AOX and TOC measurements for the neutral, phenolic, acidic, polar, hydrophilic, and volatile fractions.

Data for the whole effluents and fractions are presented as bar graphs in Figures 2 through 7. The data for effluent fractions were interpreted in terms of their Cl/C_{100} values and their relative sizes, expressed as a percentage of total TOC. The Cl/C_{100} is of interest as a likely predictor of lipophilicity and toxicity within certain fractions.

Whole Effluents

Data for the whole effluents are presented in Table III. The whole effluents contain 3.8-7.0 kg/t TOC and 0.1-0.4 kg/t AOX, depending on the stage and initial D stage pH.

Figure 2 compares mean effluent TOC from OD(EO) bleaching with the D stage begun at pH 4 (D-pH 4 bleaching) and from the same sequence with the D stage begun at pH 2 (D-pH 2 bleaching). In the D stage, D-pH 4 bleaching produces more effluent TOC. There is no increased TOC production in the (EO) stage following D-pH 4 bleaching. A reduced kappa number is observed for the pulp from D-pH 4 bleaching, and could correspond to the higher level of TOC in the D stage effluent. The delignification of the pulp is discussed later in more detail.

Figure 3 presents a comparison of mean Cl/C_{100} for the whole effluents. Both the D and (EO) stage effluents have a greater Cl/C_{100} when D-pH 2 bleaching is done, indicating a greater tendency for chlorine substitution reactions at pH 2.

The increased level of substitution by chlorine on organic material at pH 2 could be the result of a shift in chlorine containing species at pH 2 versus pH 4. Kolar and co-workers (29) reported that the sum of Cl_2 and HOCl during ClO_2 bleaching at pH 2.5 was increased compared with similar bleaching at pH 4.5. Since Cl_2 and HOCl are responsible for chlorine substitution reactions (30, 31), an overall reduction in the level of these species would result in less substitution by chlorine atoms on organics.

Ether Soluble Fraction

Table IV presents detailed data for the ether soluble fraction. This fraction contains 0.3-0.7 kg/t TOC, representing 6-12% of the total TOC, and 0.01-0.08 kg/t AOX, representing 14-23% of the total AOX.

Figure 4 presents the mean ether soluble TOC as a percentage of total TOC for both pH levels. The mean TOC produced by D-pH 4 bleaching is greater for each stage.

Figure 5 similarly compares both pH levels with respect to Cl/C_{100}. The ether soluble fraction is chlorinated to a larger extent in both the D and (EO) stages when D-pH 2 bleaching is done. An increased sum of Cl_2 and HOCl present under the pH 2 conditions is probably again responsible.

Since there is more ether soluble material formed by D-pH 4 bleaching and that material is chlorinated to a reduced extent, the overall AOX remains essentially constant under both sets of conditions. This trend is observed in other ether extractable fractions as well (28).

Phenolic Fraction

Detailed results of the analysis of the phenolic fraction are shown in Table V. The phenolic fraction contains 0.02-0.05 kg/t TOC or 0.5-0.7% of the total TOC, and 0.002-0.003 kg/t AOX or 0.8-2.6% of the total AOX.

Figure 6 compares the phenolic TOC as a percentage of total TOC for the two pH levels. In both the D and (EO) effluents, the phenolic fraction represents a higher percentage of the total TOC when the D stage is conducted at an initial pH of 4. Figure 7 shows the effect of pH on Cl/C_{100}. A decreased phenolic Cl/C_{100} is seen in the D-pH 4 case.

Degree of Delignification

The D stage effluent contains more TOC when the D stage is conducted at an initial pH of 4. The kappa number of the extracted pulp is reduced to 3.7 under D-pH 4 conditions compared with 4.3 under D-pH 2 conditions. Although this may appear to be an unusual result, similar results have been reported for O_2 delignified pulp (6). Delignification may be greater still if higher D stage consistencies were used (4).

The D+(EO) stage TOC, the kappa numbers, the change in pulp kappa number, and the ratio of TOC to kappa change are all given in Table I for the two pH levels. Although the D stage begun at pH 4 appears to give slightly increased TOC per unit kappa decrease, a possible indication of greater carbohydrate loss (26), the apparent difference is not statistically significant.

In D-pH 4 bleaching more delignification or kappa reduction can be done because less of the oxidizing power of ClO_2 may be wasted on reactions such as chlorine substitution and chlorate (ClO_3^-) formation. These reaction types are "dead ends" to bleaching.

A reaction byproduct of the oxidation of lignin by ClO_2 is chlorite ion (ClO_2^-) which may form chlorate or chlorine dioxide, depending on conditions, by the following reaction scheme (32, 33):

$$Cl_2 + ClO_2^- \longrightarrow Cl^- + [Cl_2O_2] \quad (1)$$

$$HOCl + ClO_2^- \longrightarrow OH^- + [Cl_2O_2] \quad (2)$$

$$[Cl_2O_2] \longrightarrow Cl^- + ClO_3^- \quad (3)$$

$$2[Cl_2O_2] \longrightarrow Cl_2 + 2ClO_2 \quad (4)$$

A possible explanation of the improved delignification achieved by starting the D stage at pH 4 is as follows. When bleaching begins at pH 4, more of the applied ClO_2 exists as ClO_2 rather than as Cl_2 and HOCl (29). Reaction of ClO_2 will result in the formation of chlorite (ClO_2^-), which is relatively unreactive at pH 4 and may therefore build up in concentration (29). However due to the formation of organic acids, the pH drops during the course of bleaching and the chlorite

becomes more reactive with HOCl and Cl_2 (reactions 1-4). The relatively high concentration of the now reactive ClO_2^-, forms a relatively high concentration of the intermediate $[Cl_2O_2]$ by reactions 1 and 2 (both first order in chlorite). The increased $[Cl_2O_2]$ concentration favors the formation of ClO_2 by reaction 4 (second order in $[Cl_2O_2]$). The result is the formation of more ClO_2, which can oxidize lignin, and minimization of ClO_3^- generation.

When bleaching begins at pH 2, ClO_2^- is reactive immediately and its concentration is therefore lower at any given time than in the pH 4 case. The result is a reduced concentration of the reactive intermediate $[Cl_2O_2]$ at any given time. The formation of chlorate is therefore favored.

Another possible explanation involves the presence of chloride ion. A possible reactive route of ClO_2^- is its acid catalyzed decomposition (33, 34):

$$4ClO_2^- + 2H^+ \longrightarrow 2ClO_2 + Cl^- + ClO_3^- + H_2O \quad (5)$$

In the presence of chloride ion, the decomposition may be approximated by:

$$5ClO_2^- + 4H^+ \longrightarrow 4ClO_2 + Cl^- + 2H_2O \quad (6)$$

When bleaching begins at pH 4, chlorite is initially unreactive by acid catalyzed decomposition until the pH decreases. Since chloride ion is rapidly formed during ClO_2 bleaching (34) its concentration is likely to increase as the pH decreases. Once chlorite becomes reactive, its acid catalyzed decomposition proceeds by reaction 6, due to the presence of chloride. Chlorate is not formed by reaction 6. The presence of chloride has been shown to limit chlorate formation in the acid catalyzed decomposition of chlorite (34).

Although these mechanisms have by no means been proven to occur, they are plausible and consistent with our observations. They result in more ClO_2 formation and less ClO_3^- formation, and may be responsible for the increased delignification observed under the conditions of this study.

EXPERIMENTAL METHODS

D Stage Bleaching

All D stages were done in a specially designed 20 L batch reactor. Bleaching was done at 2% consistency, at 45°C, for 30 minutes, and at a kappa factor of 0.25. The mixer was run at 350 rpm.

(EO) Stage Bleaching

All (EO) stages were done in a Quantum Technologies high shear mixer at 10% consistency, at 70°C, and for 70 minutes. The NaOH charge was 0.55 times the total active chlorine charge; the O_2 charge was 0.5% on pulp; and 4.1% of the total D stage filtrate was included as carryover. The slurry was mixed at 15 hertz for 3 seconds, every 5 minutes.

Effluent Preparation

The D stage effluent was collected by filtration of the 2% slurry; the (EO) stage effluent was similarly collected after the 10% slurry was diluted to 2%. This was done to maintain a similar TOC content in all effluents for ether extraction. Effluent samples were filtered to remove any fibers, quenched with excess sodium sulfite, and acidified to a pH of less than 2. Ether extractions were always started within 2 days of effluent collection.

Ether Extraction of Effluents

Ether extraction was done on 4 L of effluent using continuous liquid-liquid extractors. Extraction was carried out with 500 ml of diethyl ether. The first ether phase was collected after 96 hours of extraction and was replaced with 500 ml of fresh ether. Extraction was continued for 336 total hours. The extraction was then stopped, and the second ether phase and the non-extractable materials were collected.

Ether Extract Fractionation

The first ether phase was diluted to 500 ml, 100 ml of the sample collected, and the remaining ether placed in a separatory funnel for fractionation. The ether was extracted 3 times with 25 ml of 0.5 M $NaHCO_3$, and the extracts were collected and acidified. The ether was next extracted 3 times with 25 ml of 0.5 M NaOH, and these extracts were also collected and acidified. The $NaHCO_3$ soluble material is the acidic fraction; the NaOH soluble material is the phenolic fraction;

and the remaining ether soluble material is the neutral fraction.

Sample Preparation

Ether was removed from all samples by evaporation to dryness, or near to dryness. The samples were then dissolved in water, acidified, and diluted to a known volume. To ensure reasonable sample recovery and to be certain the ether was removed, TOC and AOX mass balances were done around the fractionation scheme.

TOC Analysis

Measurement of TOC was done using a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate. Samples were prepared for TOC analysis by acidifying them, and sparging for 5 minutes with nitrogen to drive off any interfering carbonate species.

AOX Analysis

Measurement of AOX was done using a Dohrman model DX-20 organic halide analyzer. Sample preparation was done by a slight modification of method SCAN-W 9:89 (35). In this case samples were shaken for 4 hours rather 1 hour, to more completely adsorb the polar fractions.

SUMMARY AND CONCLUSIONS

An oxygen-bleached softwood kraft pulp was delignified to a greater extent by the OD(EO) sequence when the D stage was run at an initial pH of 4 than when the initial pH was 2. D-pH 4 bleaching resulted in greater percentages of the total TOC appearing in the environmentally significant ether soluble and phenolic fractions. However, the material in these fractions was substituted by chlorine atoms to a reduced extent under D-pH 4 conditions. The net result was similar amounts of AOX in these fractions at both pH levels.

Since D-pH 4 bleaching causes increased D stage delignification, an equivalent amount of delignification can be done with less applied chemical, and an economic gain achieved. A reduced ClO_2 charge will result in less effluent AOX, and may also provide environmental benefits.

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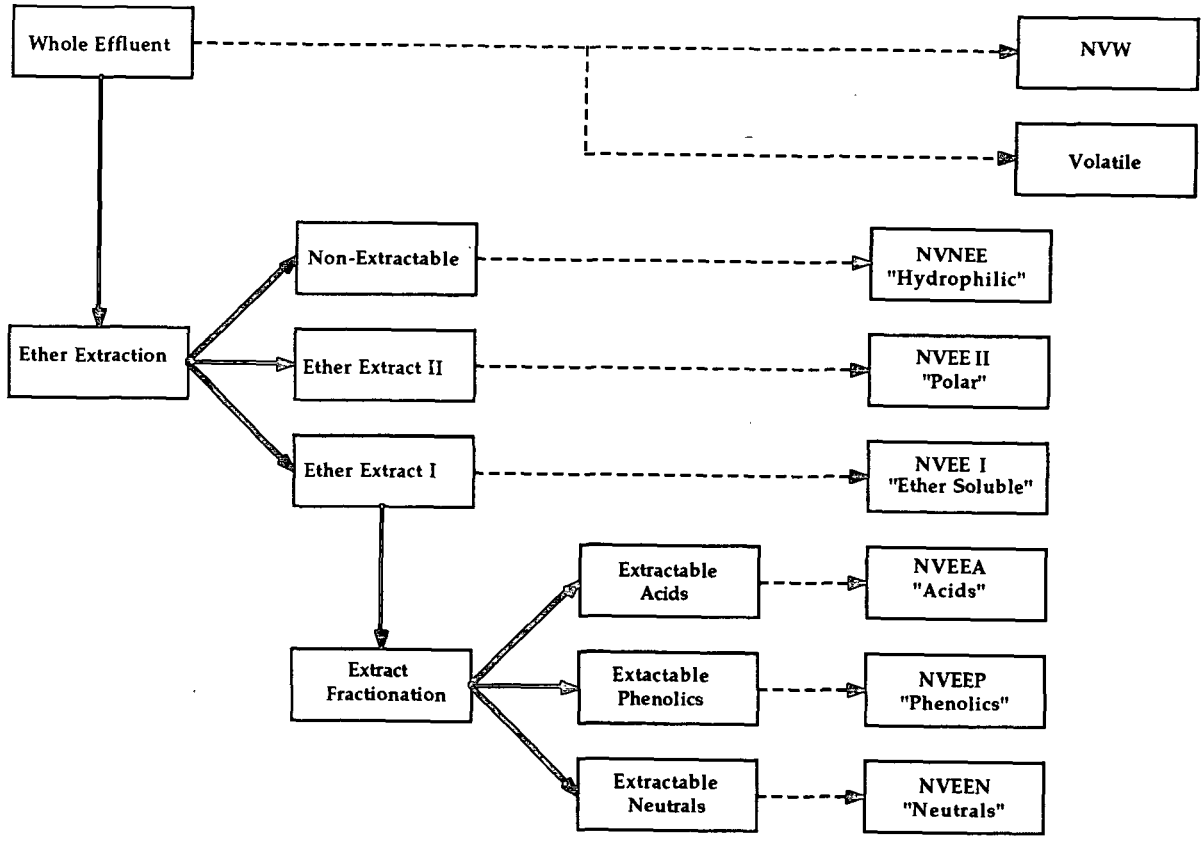
Figure 1. Effluent Fractionation.



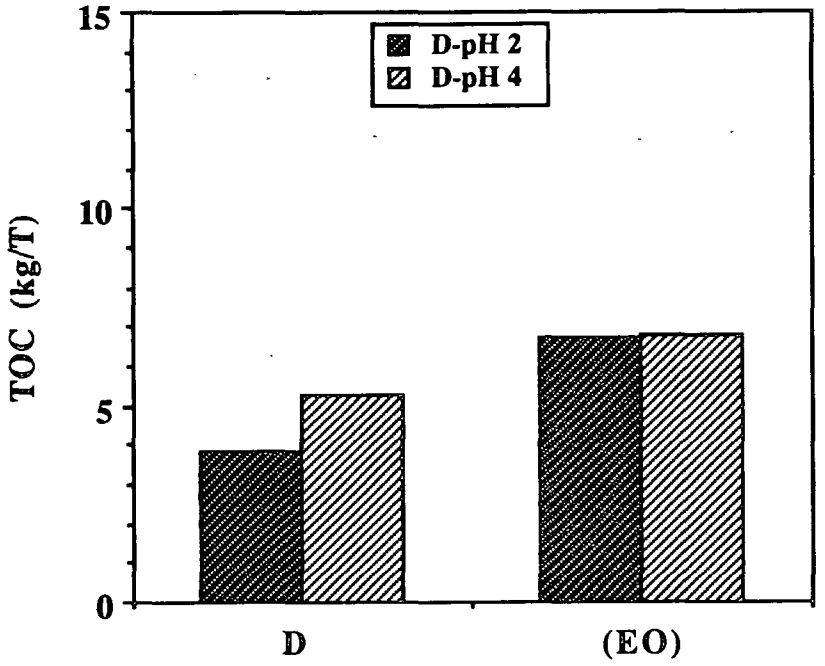


Figure 2. Whole Effluent TOC.

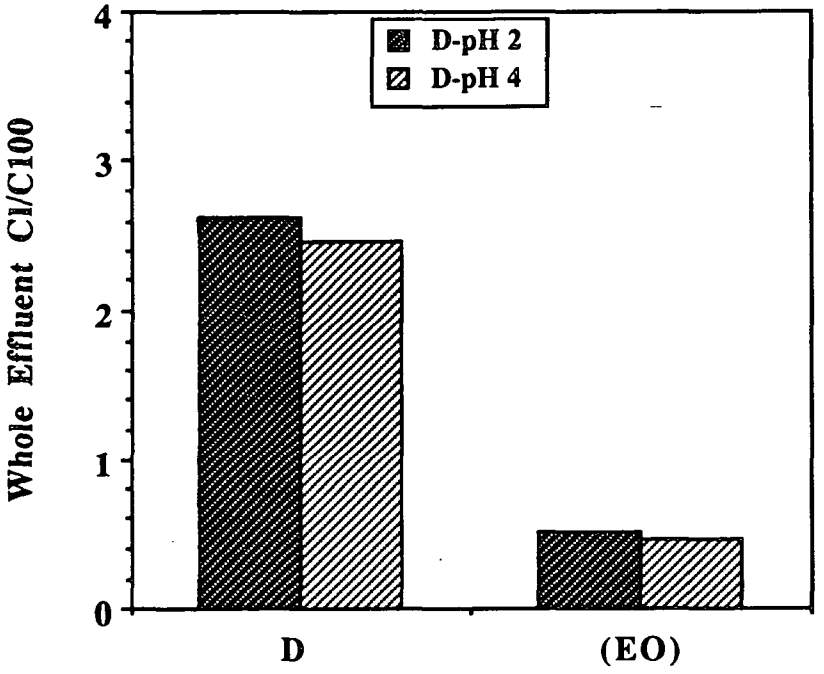


Figure 3. Whole Effluent Cl/C100.

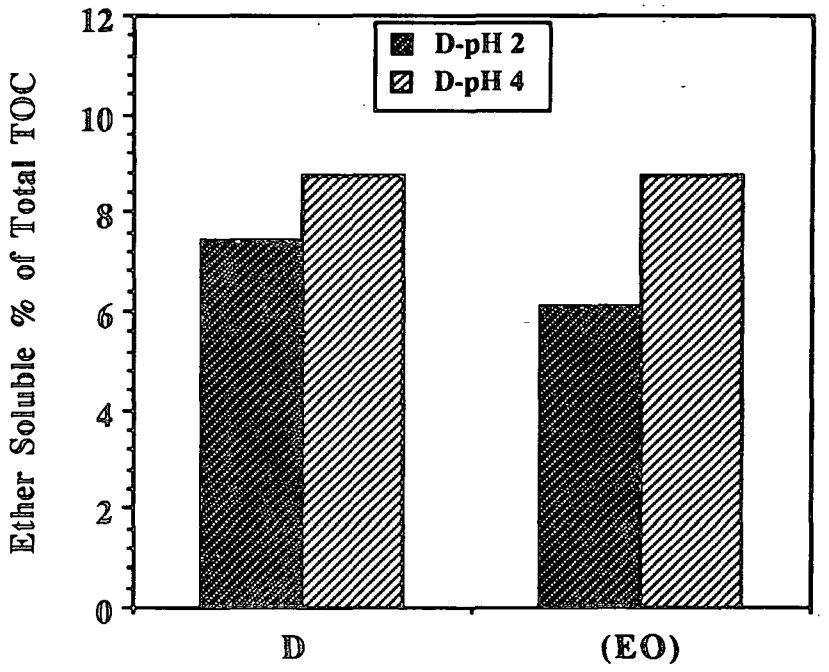


Figure 4. Ether Soluble TOC, as % of Total.

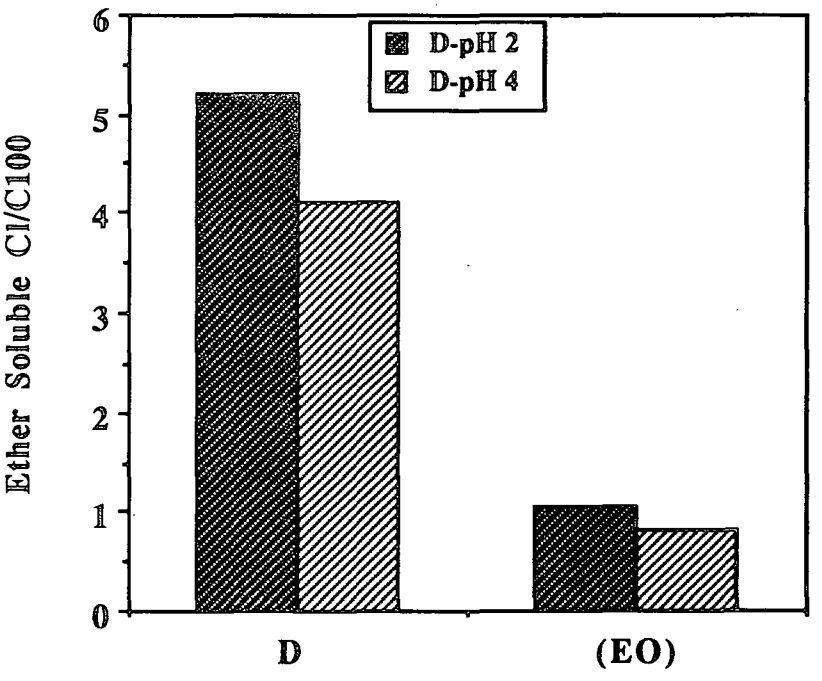


Figure 5. Ether Soluble Cl/C100.

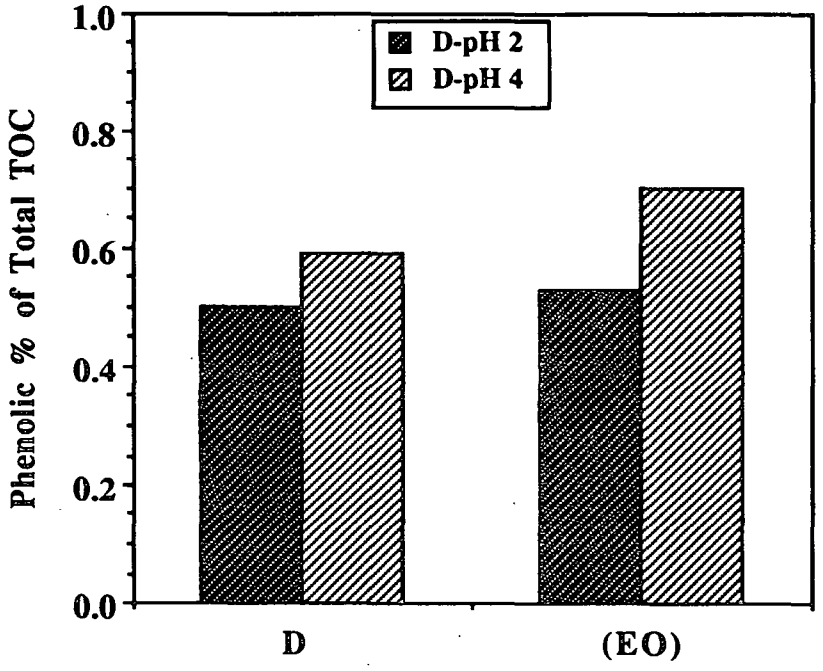


Figure 6. Phenolic TOC, as % of Total.

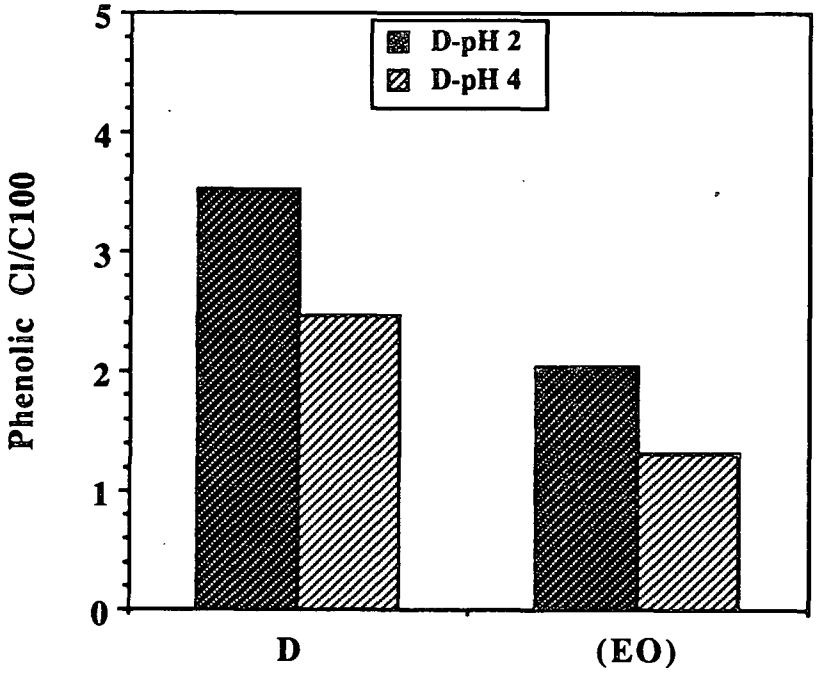


Figure 7. Phenolic Cl/C100.

Table I. D+(EO) TOC and Kappa Number Data for OD(EO) Sequence.

D Stage Type	D + (EO) TOC (kg/t)	Kappa Number	Δ kappa	TOC/Δ kappa
D-pH 2	10.6	4.23	9.87	1.07
	10.4	4.44	9.66	1.08
D-pH 4	12.4	3.70	10.40	1.19
	11.7	3.71	10.39	1.13

Table II. Effluent Fraction Codes and Descriptions of Fractions.

Fraction Code	Description
NVW	Non-volatile, whole.
NVNEE	Non-volatile, non-ether extractable ("Hydrophilic").
NVEE II	Non-volatile, difficult to extract with ether ("Polar").
NVEE I	Non-volatile, readily ether extractable ("Ether Soluble").
NVEEA	Non-volatile, ether extractable acidic compounds ("Acids").
NVEEP	Non-volatile, ether extractable phenolic compounds ("Phenolics").
NVEEN	Non-volatile, ether extractable neutral compounds ("Neutrals").

Table III. Whole Effluent and Summed Fraction Characteristics.

D Stage	D-pH 2		D-pH 4	
TOC, kg/t	3.85	3.80	5.37	5.17
Total TOC[a], kg/t	4.43	4.29	5.55	6.64
AOX, kg/t	0.299	0.294	0.381	0.386
Total AOX[a], kg/t	0.297	0.264	0.337	0.336
Cl/C_{100}	2.63	2.61	2.40	2.53
(EO) Stage				
TOC, kg/t	6.79	6.60	7.01	6.54
Total TOC[a], kg/t	6.70	6.52	6.99	7.60
AOX, kg/t	0.101	0.102	0.0943	0.0929
Total AOX[a], kg/t	0.0938	0.0930	0.0983	0.0877
Cl/C_{100}	0.50	0.52	0.45	0.48

[a]Sum of corresponding values for volatile, hydrophilic, polar, acid, phenolic, and neutral fractions.

Table IV. Ether Soluble Fraction.

D Stage	D-pH 2		D-pH 4	
TOC, kg/t	0.383	0.267	0.643	0.388[a]
% of total TOC	8.65	6.22	11.6	5.85[a]
AOX, kg/t	0.0547	0.0439	0.0773	0.0474
% of total AOX	18.4	16.6	22.9	14.1
Cl/C_{100}	4.83	5.56	4.07	4.13[a]
(EO) Stage				
TOC, kg/t	0.406	0.399	0.532	0.748
% of total TOC	6.06	6.12	7.61	9.84
AOX, kg/t	0.0127	0.0125	0.0150	0.0154
% of total AOX	13.5	13.4	15.3	17.6
Cl/C_{100}	1.06	1.06	0.95	0.69

[a]Determined from TOC balances. Sample was contaminated during evaporation.

Table V. Phenolic Fraction.

D Stage	D-pH 2		D-pH 4	
TOC, kg/t	0.0239	0.0198	0.0325	0.0389
% of total TOC	0.54	0.46	0.59	0.59
AOX, kg/t	0.00255	0.00201	0.00273	0.00239
% of total AOX	0.86	0.76	0.81	0.71
Cl/C_{100}	3.60	3.45	2.84	2.07
(EO) Stage				
TOC, kg/t	0.0364	0.0341	0.0513	0.0502
% of total TOC	0.54	0.52	0.73	0.66
AOX, kg/t	0.00243	0.00180	0.00216	0.00177
% of total AOX	2.59	1.94	2.20	2.02
Cl/C_{100}	2.26	1.79	1.42	1.19

Section 4 Conclusions

Effluents from the OD(EO) partial bleaching sequence, with the D stage begun at 2 different pH levels, were compared using the ether extraction based effluent fractionation.

Based on the composition of environmentally significant effluent fractions, neither initial D stage pH level appeared to represent an advantage from an environmental point of view. The OD(EO) sequence with the D stage begun at pH 2, produced a smaller proportion of material within the environmentally significant ether soluble and phenolic fractions than the sequence with the D stage begun at pH 4. However, at pH 2 the ether soluble and phenolic material was substituted to an increased extent by chlorine atoms. The result was a similar quantity of ether soluble and phenolic AOX in both cases.

The D stage begun at pH 4 achieved greater delignification than the pH 2 case. To achieve the same delignification, less ClO_2 per unit of lignin must therefore be applied when the D stage is begun at pH 4, and all organic material will be substituted by fewer chlorine atoms. This could represent an environmental advantage in addition to cost savings associated with the decreased ClO_2 use.

Section 5: The Effect of D Stage Reaction Time on the Characteristics of Whole Effluents and Effluent Fractions from D(EO) Bleaching of Oxygen Delignified Softwood Kraft Pulp

Section 5 compares effluents from the OD(EO) bleaching sequence with the D stage duration varied between 3 seconds and 30 minutes. The ether extraction based fractionation is the basis for effluent characterization.

The OD(EO) bleaching sequence utilizing short duration D stages (one minute or less) had 3 advantages from an environmental point of view. The sequence using a short duration D stage produced a smaller proportion of material within the environmentally significant ether soluble fraction. In addition, that material was substituted by chlorine atoms to a reduced extent. Also with a 1 minute duration D stage, the proportion of ether soluble AOX (presumed to be "bad" AOX) reached a sharp minimum. These effects were most likely caused by the acidic subfraction of the ether soluble material, since the same trends in the data were observed there.

Short reaction times, in addition to providing possible environmental benefits, provided up to 85% of the delignification that occurred at extended times. At these same short reaction times, only 40% of the overall AOX was formed. Since the level of AOX at short D stage reaction times was near that of proposed AOX limits, the OD(EO) sequence with a short duration D stage may allow compliance.

THE EFFECT OF D STAGE REACTION TIME ON THE CHARACTERISTICS OF WHOLE EFFLUENTS AND EFFLUENT FRACTIONS FROM D(EO) BLEACHING OF OXYGEN DELIGNIFIED SOFTWOOD KRAFT PULP

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ABSTRACT

The effect of D stage reaction time on the characteristics of effluents and effluent fractions from D(EO) bleaching of oxygen delignified softwood kraft pulp is considered in this paper. Effluents from the OD(EO) sequence with D stage reaction times of 3 seconds, 1 minute, 5 minutes, and 30 minutes were fractionated and characterized. The fractionation consisted of ether extraction and separation of the extract into acidic, phenolic, and neutral subfractions. Adsorbable organic halide (AOX) and total organic carbon (TOC) were determined for the whole D and (EO) effluents as well as for the fractions from each stage. Each fraction was characterized in terms of its chlorine to carbon ratio (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}) and in terms of the proportions of the total TOC and AOX contained within it.

A D stage of only 3 seconds duration resulted in 67% of the delignification achieved in a 30 minute stage. The 3 second D stage resulted in only 26% as much AOX and 34% of the Cl/C_{100} given by the 30 minute D stage. A one minute D stage achieved 84% of the delignification while generating only 42% of the AOX and 51% of the Cl/C_{100} of the 30 minute stage.

The Cl/C_{100} of all effluent fractions except the neutral fraction was reduced when the D stage was shortened from 30 minutes to 3 seconds. The extent of this reduction was different for the different fractions. In addition to a sharp Cl/C_{100} reduction in the environmentally significant ether soluble fraction, the proportion of ether soluble TOC was reduced at short D stage reaction times, and the proportion of the total AOX found in the ether soluble fraction reached a minimum value at 1 minute of D stage reaction time. These effects are primarily due to the acid subfraction of the ether soluble material. A bleaching sequence with a very short D stage or a low kappa factor D stage may therefore possess environmental advantages in addition to an overall AOX reduction.

INTRODUCTION

In the area of pulp bleaching, environmental issues continue to gain importance relative to more conventional concerns such as efficiency of delignification and economics. The threat of extremely low AOX limits and consumer demand have already led many mills to substantially reduce their AOX discharge by a variety of methods including improved brownstock washing (1-3), extended Kraft delignification (4-6), oxygen delignification (1, 4, 7, 8), substitution of chlorine dioxide for chlorine (4, 7, 9-14), and oxidative caustic extraction (9, 15-17).

Although these methods reduce AOX, it remains uncertain what effect they have on the environment, because AOX reduction does not necessarily mean the environmental impact is reduced (18, 19). On the other hand, it may be somewhat irrelevant whether AOX reduction actually affects the environment, due to impending regulation.

Levels of AOX in proposed regulations may not be achievable using chlorine containing bleaching agents. However, both chlorine dioxide bleaching and oxygen delignification offer more environmental benefits over conventional chlorine bleaching than the AOX reduction alone suggests (20). Since conversion to totally chlorine free bleaching processes is not yet a viable alternative for most pulp producers, bleaching with chlorine dioxide is worth further study. If such a system can be optimized with respect to certain process variables, perhaps the required AOX reduction may be achieved and the environmental effects of the sequence minimized as well. The effect of D stage pH on the characteristics of whole effluents and effluent fractions from D(EO) bleaching of oxygen delignified softwood kraft pulp has been previously investigated (21) using an effluent fractionation based on ether extraction (20).

Another D stage process variable which may be expected to impact the nature of the effluent is reaction time. Removal of lignin and substitution on organic material by chlorine during chlorine dioxide treatment would be expected to have different time dependence,

since the two processes occur by different mechanisms (22, 23). A variety of bleaching studies have considered the effect of reaction time on lignin removal in the chlorination of kraft pulps (24-30), in the chlorine dioxide prebleaching of kraft pulps (31), and in the prebleaching of kraft pulps with various combinations of chlorine and chlorine dioxide (32, 33). However, none of these studies has considered the effect of reaction time on the nature of the effluents.

Pulp bleaching effluents in general have been characterized with respect to adsorbable organic halide (AOX) (34-38) and in terms of individual compounds or environmentally significant groups of compounds such as chlorophenolics (34, 39-46), chlorinated dioxins (43, 47, 48), chlorinated neutral compounds (46, 49, 50), chlorinated carboxylic acids (46, 51), and chloroform (42, 52). However because of the complexity of pulp bleaching effluents, these analyses give an incomplete picture of their likely environmental effects.

A preferable alternative is summative analysis of the effluent by fractionation into meaningful classes of compounds, followed by relevant characterization of the fractions. One such procedure, based on ether extraction, has been developed and applied to effluents (20, 21). Ether extraction was chosen as the basis for this procedure because virtually all effluent components known to be significant from an environmental standpoint are found in the extracts. For example, the ether extract contains low molecular weight material (53, 54) which may correlate with acute and chronic toxicity (19, 55, 56). The ether extract exhibits most of the effluent's mutagenicity (49, 57, 58) and toxicity (53) and contains environmentally significant compounds such as chlorophenolics (44, 59) and chlorinated neutral compounds (50, 60). Chlorine to carbon ratios (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}), which may be expected to correlate with environmental behavior, were determined for the fractions. Within certain effluent fractions the ratio of chlorine to carbon atoms may predict acute toxicity (39, 59), chronic toxicity (61), and lipophilicity (62). These fractionation and characterization methods were used for the present study of the effect of D stage reaction time on D(EO) bleaching of oxygen delignified softwood kraft pulp.

EXPERIMENTAL APPROACH

Pulp Bleaching

A mill-produced, oxygen-bleached kraft pulp with a kappa number of 14.1 was bleached by a D(EO) sequence in the laboratory. D stage reaction times of 3 seconds, 1 minute, 5 minutes, and 30 minutes were considered. The D stages were quenched with excess sodium sulfite after the appropriate bleaching time. Only the first two stages of bleaching were done, since most of the delignification and therefore most of the effluent load production occurs in these stages. The D stages were done in a specially designed batch reactor, and the (EO) stages were done in a high shear mixer. Kappa numbers after bleaching are given in Table I.

A schematic diagram of the D stage bleaching reactor used in this study is given in Figure 1. The reactor was specially designed to bleach pulp for short periods of time, to quench the reaction after a given time interval, and to produce sufficient quantities of effluent for analysis. This batch reactor allowed consistencies of 2% and reaction times as short as 3 seconds.

The reactor consists of a thermostatted 20 L cylindrical reaction chamber with chemical injection cylinders on 3 sides of it. During a typical bleaching experiment only 2 of the injection cylinders were used: one for the bleaching agent, one for the quench. During such experiments a pulp slurry of the appropriate consistency, pH, and temperature is put in the mixing chamber. The mixing chamber is initially separated from the injection cylinders by teflon rupture membranes. The cover, equipped with a teflon-coated mixer, is attached and the chemicals added to the cylinders. Once the pulp is mixing at 350 rpm the bleaching agent is injected, through the membrane by an air-driven piston, into the slurry. At this point the consistency is 2%. The injection of chlorine dioxide triggers a timer which automatically injects the quench after the appropriate time.

Based on work by Liebergott and coworkers (27) the mixing rate of 350 rpm should be sufficient to insure uniform bleaching with aqueous bleaching agents. Data showing no effect of mixing on reaction rate (27, 29) suggest that bulk phase diffusion does not limit the reaction rate. During a preliminary mixing study done at only 250 rpm, high speed videotape demonstrated that mixing was complete in about 0.5 seconds.

Effluent Fractionation and Characterization

The effluents produced in this study were fractionated by ether extraction. To measure Cl/C_{100} on the ether extract and its fractions, the ether was exhaustively removed by evaporation, and AOX and TOC were then measured on each fraction. During evaporation, volatiles other than ether were also removed. To obtain information on the volatile fraction, a sample of the whole effluent was similarly evaporated and the carbon and chlorine losses determined.

Figure 2 depicts the effluent fractionation scheme, and Table II lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions: a non-extractable fraction and two ether extractable fractions. The first ether fraction is the most non-polar of the extractable material and is readily extracted, while the second is more polar and is removed slowly over an extended period. The first ether fraction was further separated into acids, phenolics, and neutrals. Each fraction was then evaporated, as represented in Figure 2 by the dashed horizontal lines, to yield the final samples.

Data Analysis

The different D stage reaction time bleaching experiments were performed in duplicate, and the effluents from the D and (EO) stages of bleaching were fractionated and analyzed separately. This resulted in two completely independent sets of data for each D stage reaction time.

Analyses of variance (AOV) were done on the data from each fraction to assess the significance of differences between D stage reaction times and between stages. Since data with high Cl/C_{100} had a greater variance than the low Cl/C_{100} data, all Cl/C_{100} data were log transformed to stabilize variance. When AOV showed a significant effect of reaction time, a least significant difference was determined using Duncan's multiple range test (63).

RESULTS AND DISCUSSION

The data for the whole effluents and for all fractions are given in Tables III-X. The total TOC and AOX (given in Table III) represent TOC and AOX mass balances around the fractionation scheme, and were determined as the sums of the AOX and TOC measurements for the neutral, phenolic, acidic, polar, hydrophilic, and volatile fractions.

Data for the pulp delignification and for the whole effluent and effluent fraction characteristics are presented graphically in Figures 3 through 16. Effluent characterization graphs consist of 3 curves based on data collected at the 4 different D stage bleaching times of 3 seconds, 1 minute, 5 minutes, and 30 minutes. The curves labeled D stage refer to the D stage effluent alone and the curves labeled (EO) stage refer to the (EO) stage effluent alone. The curves labeled D + (EO) stage refer to the combined data from the D and (EO) stages, not to measurements on combined filtrates. The D, (EO), and D + (EO) designations apply to the data tables as well.

The data for individual fractions were interpreted in terms of their Cl/C_{100} values and their relative sizes, expressed as a percentage of total TOC or AOX. The Cl/C_{100} is of interest as a likely predictor of lipophilicity and toxicity within certain fractions.

Degree of Delignification

The effect of D stage reaction time on delignification (expressed as DE Kappa number) is shown in Figure 3 and the data are given in Table I. D stage bleaching for only 3 seconds results in a Kappa number decrease from 14.1 to about 7.8, or 67% of the Kappa number reduction that occurs in 30 minutes. One minute of D stage bleaching results in about 84% of the total 30 minute kappa number reduction, or a DE Kappa number of about 6.2. This shows that in conventional bleaching the greater part of the lignin is made soluble after only a very short time, and undergoes further reaction with chlorine containing chemicals for an extended period. This results in increased chlorine substitution on the organics as reaction time increases.

In addition to the kappa number data, Table I shows the sum of the TOC values for the D and (EO) effluents and the TOC per unit of Kappa number decrease, for the different D stage reaction times. Although at 3 seconds the mean $TOC/\Delta Kappa$ is higher than at the other D stage times, the difference is not large enough to be considered statistically significant.

Whole Effluents

Data for the whole effluents are presented in Table III. The whole effluents contain 2.2-7.0 kg/t TOC and 0.04-

0.40 kg/t AOX, depending on the stage and on the D stage reaction time.

Figure 4 shows the effect of D stage reaction time on effluent TOC content. The D stage TOC and the overall D + (EO) stage TOC increase with increasing reaction time. The (EO) stage TOC remains relatively constant at all reaction times. The D stage effluent TOC formation and the Kappa number reduction are virtual mirror images (Figure 5) indicating that the increased delignification seen at longer reaction times is due to increased D stage delignification, not (EO) stage delignification.

The amount of (EO) stage TOC formed at 3 seconds is almost identical to the amount formed at 30 minutes of D stage reaction time. This indicates that lignin removal in the latter part of the D stage and (EO) stage lignin removal may be parallel reaction sequences operating independently rather than sequential reactions, since after 3 seconds D stage reaction time has little or no effect on (EO) stage delignification.

Figure 6 shows the effect of D stage reaction time on the whole effluent Cl/C_{100}. While 67% of the delignification is seen after 3 seconds in the D stage, the overall Cl/C_{100} in the effluent is only about 34% of that seen after 30 minutes of D stage bleaching. AOX produced with the 3 second D stage is only 26% of that produced using a 30 minute D stage. Similarly a one minute D stage achieves 84% of the delignification while generating only 42% of the AOX and 51% of the Cl/C_{100} of the 30 minute stage. Short reaction times favor lignin removal over substitution of chlorine atoms onto organic material. The whole effluent Cl/C_{100} approaches an asymptotic level as D stage reaction time increases.

Ether Soluble Fraction

Table IV presents detailed data for the ether soluble fraction. It contains 0.2-0.9 kg/t TOC, representing 7-20% of the total TOC, and 0.01-0.10 kg/t AOX, representing 14-36% of the total AOX. The ether soluble fraction contains low molecular weight compounds that are non-polar in nature.

The mean ether soluble TOC, expressed as a percentage of the total TOC, is shown in Figure 7 for all D stage reaction times. For both the D and (EO) stage effluents, a greater proportion of the TOC is ether soluble when the D stage is 30 minutes long than when it is of short duration. Increased reaction time may allow further fragmentation of already solublized lignin, resulting in a lower molecular weight material and more ether soluble TOC. Although the D stage effluent appears to have a maximum proportion of ether soluble TOC at 1 minute of reaction time and the (EO) stage effluent a minimum, the overall D + (EO) proportion of ether soluble TOC increases to an asymptotic level with increased D stage reaction time.

Figure 8 shows the ether soluble Cl/C_{100} for the different D stage reaction times. Increased D stage reaction time generally results in increased Cl/C_{100} in the ether soluble fraction for both stages. Increased levels of chlorine substitution and associated decreases in water solubility may be responsible, in part, for the increase in the size of the ether soluble fraction at longer D stage reaction times. After 3 seconds of D stage bleaching, the overall D + (EO) Cl/C_{100} value is only about 38% of its value at 30 minutes, although about two-thirds of the delignification occurs. A one minute D stage results in only 29% of the ether soluble AOX and 43% of the Cl/C_{100} of the 30 minute D stage, yet 84 % of the delignification is done.

The proportion of ether soluble AOX present in the effluents produced by the various D stage reaction times is shown in Figure 9. A minimum proportion of ether soluble AOX (presumed to be "bad" AOX) occurs in effluents produced using the 1 minute D stage. A similar trend is evident in both the D and (EO) stage effluents.

Within the ether soluble fraction, a reduced D stage reaction time may have several benefits of an environmental nature: a substantially reduced Cl/C_{100} for the ether soluble material, a reduced proportion of ether soluble TOC, and a minimum proportion of ether soluble AOX. Based on these results the potential environmental effects of the OD(EO) sequence may be minimized by running the D stage for 1 minute or less.

Polar Fraction

Detailed results for the polar fraction, or that material which is extracted slowly by ether, are shown in Table V. The phenolic fraction contains 0.1-0.8 kg/t TOC or 4-12% of the total TOC, and 0.002-0.04 kg/t AOX or 3-15% of the total AOX. The material contained within this fraction is likely to be low molecular weight and more polar than that within the ether soluble fraction.

Although no increase in the proportion of polar TOC is seen as D stage reaction time increases, the Cl/C_{100} increases at longer reaction times, as shown in Figure 10. At 3 seconds, the overall D + (EO) polar Cl/C_{100} is only about 19% of that which occurs at 30 minutes.

Hydrophilic Fraction

Complete data on the hydrophilic fraction are given in Table VI. The fraction contains 2-5 kg/t TOC (70-85% of the total TOC) and 0.03-0.16 kg/t AOX (41-77% of the total AOX). Material within the hydrophilic fraction is either very polar or of high molecular weight relative to the extractable fractions.

No trend in the proportion of TOC within this fraction is seen with increasing D stage reaction time. However, the Cl/C_{100} increases at longer D stage reaction times, as shown in Figure 11. The overall D + (EO) hydrophilic Cl/C_{100} is only 36% of it's 30 minute value after 3 seconds of D stage reaction time.

It is interesting to note that both the polar and hydrophilic fraction D stage Cl/C_{100} values exhibit relative maxima at 1 minute of D stage reaction time, corresponding to the apparent minimum seen within the D stage ether soluble Cl/C_{100}. This is consistent with the steadily increasing whole D stage effluent Cl/C_{100} and lends additional credibility to the data.

Acid Fraction

Table VII presents the detailed results for the acid subfraction of the ether soluble material. About 0.15-1.2 kg/t TOC, representing 6-18 % of the total TOC and 0.006-0.10 kg/t AOX, representing 12-31% of the total AOX, is contained within this fraction. The acid fraction is likely to include both chlorinated and non-chlorinated resin acids, fatty acids, benzoic acid derivatives, and various mono- and dibasic carboxylic acids.

Increased D stage reaction time generally results in an increased proportion of acidic ether soluble TOC, as shown in Figure 12. The increased proportion of ether soluble TOC (shown previously) is accounted for by the acid fraction, since the proportions of phenolic and neutral TOC do not change with D stage reaction time. The acid fraction Cl/C_{100} increases to an asymptotic level with D stage reaction time, as shown in Figure 13. The overall Cl/C_{100} at 3 seconds is only 30% of that at 30 minutes. The minimum in the proportion of ether soluble AOX is also likely to be due to the acid fraction's contribution to the ether soluble material.

Figure 14 shows an apparent minimum proportion of acid fraction AOX at 1 minute of D stage reaction time, as was seen for the ether soluble fraction.

A reduction in D stage reaction time appears to have several benefits within the acid fraction: a substantially reduced Cl/C_{100}, a reduced proportion of acid fraction TOC, and a minimum proportion of acid fraction AOX. Although the acid fraction is not considered the most potentially harmful subfraction of the ether soluble material since it is the most polar portion, it is nevertheless the largest component of the environmentally significant ether soluble fraction, and improvements within this fraction are therefore of interest.

Phenolic Fraction

Complete data for the phenolic fraction are shown in Table VIII. The fraction contains 0.02-0.06 kg/t TOC or 0.6-1.0% of the total TOC, and 0.001-0.003 kg/t AOX or 0.9-2.3% of the total AOX. The phenolic fraction is likely to contain both chlorinated and non-chlorinated phenols, guaiacols, vanillins, and other degradation fragments with phenolic functionality.

The duration of the D stage does not affect the proportion of phenolic TOC. On the other hand, the Cl/C_{100} of this fraction increases with D stage reaction time as shown by Figure 15. The effect appears to be smaller in the phenolic fraction than in the other fractions (for example the acid fraction) since the phenolic Cl/C_{100} reaches an asymptotic level at a shorter D stage reaction time. The overall reduction in the extent of the Cl/C_{100} from 30 minutes to 3 seconds (49%) is less in this case, but still an important reduction since this is an environmentally significant fraction.

Neutral Fraction

Table IX presents the entire data set for the neutral fraction of the ether soluble material. This fraction contains 0.02-0.06 kg/t TOC (0.4-4.8% of the total TOC) and 0.0006-0.0030 kg/t AOX (0.8-2.4% of the total AOX). Contained within the neutral fraction are chlorinated and non-chlorinated thiophenes, benzene derivatives, enollactones, furanones, pyrones, dimethyl sulfones, and various hydrocarbons.

The proportion of neutral fraction TOC is not affected by D stage reaction time. As shown by Figure 16, there is no clear reduction in neutral fraction Cl/C_{100} with reduced D stage reaction time as occurred in

other fractions. However the Cl/C_{100} at 1 minute is significantly reduced versus that at 5 minutes. This fraction was the most difficult to work with, because of its small size and hydrophobic nature. Consequently, the data exhibit considerable scatter. Nevertheless, it is very interesting that both the D and (EO) stage curves are nearly identical. The reproducibility of these graphs lends some credibility to the data within them.

Volatile Fraction

There are no significant time related effects observed in the volatile fraction data, due to scatter and incomplete data. The data set is included here (Table X) for the purposes of a complete analysis, however. Volatile compounds present may include chloroform, methanol, and acetic acid.

Practical Implications

A major practical implication of this work is that a sequence with a very limited D stage (3 seconds long) removes two-thirds of the material removed by a sequence with a 30 minute D stage, while reducing the D + (EO) stage AOX to only 26% of that formed by a sequence with a 30 minute D stage. Similarly, a one minute D stage results in 84% of the lignin removal with only 51% of the AOX production. Since (EO) stage lignin removal is unaffected by the extent of the D stage, limiting the D stage, either in time or perhaps in level of charge, may allow compliance with AOX regulation if the remaining lignin can be removed by other means. Possible methods of removal may be additional oxidative enhancement of the caustic extraction stages or a second, very limited chlorine dioxide delignification stage prior to brightening. A second delignification stage would have minimal impact on the effluent since most lignin is already removed, and a small ClO_2 charge would be applied. Concurrently with this work it has been shown that high brightness can be achieved, using the very limited kappa factor of 0.05 in the D stage (64). In this case the stages after the D stage were strengthened to achieve supplemental delignification.

A second practical implication of this work is that such a limited D stage would require no bleach tower, simply a mixer and a length of pipe for retention. Since towers are not needed, an additional chlorine dioxide delignification stage could be installed at a much lower capital cost than a conventional stage.

EXPERIMENTAL METHODS

Pulp Bleaching

A mill-produced, 14.1 kappa O_2-delignified southern softwood kraft pulp was used in this study. The pulp was collected just after the O_2 stage and was well washed before bleaching.

D Stages

All D stages were done in a specially designed 20 L batch reactor. Bleaching was done at 2% consistency, at 45°C, and at a kappa factor of 0.25. The mixer was run at 350 rpm. Initial pH was adjusted to 2 by the addition of sulfuric acid solution. A 13 g/L solution of sodium sulfite was used for D stage quenching. After quenching with 1.5 L of the sulfite solution, the D stage slurry was at about 1.8% consistency.

(EO) Stages

All (EO) stages were done in a Quantum Technologies high shear mixer at 10% consistency, at 70°C, and for 70 minutes. The NaOH charge was 0.55 times the total active chlorine charge; the O_2 charge was 0.5% on pulp; and no carryover was added since it contained sodium sulfite . Addition of O_2 pressurized the mixer to about 20 psig. The slurry was mixed at 15 hertz for 3 seconds, every 5 minutes.

Effluent Preparation

The D stage effluent was collected by filtration of the 1.8% slurry; the (EO) stage effluent was similarly collected after the 10% slurry was diluted to 1.8%. This was done to maintain a similar TOC content in all effluents for ether extraction. Effluent samples were filtered to remove any fibers and acidified to a pH of less than 2. Ether extractions were always started within 2 days of effluent collection.

Ether Extraction of Effluents

Ether extraction was done on 4 L of effluent using continuous liquid-liquid extractors. Extraction was carried out with 500 ml of diethyl ether. The first ether phase was collected after 96 hours of extraction and was replaced with 500 ml of fresh ether. Extraction was continued for 336 total hours. The extraction was then stopped, and the second ether phase and the non-extractable materials were collected.

Ether Extract Fractionation

The first ether phase was diluted to 500 ml, 100 ml of the sample collected, and the remaining ether placed in a separatory funnel for fractionation. The ether was extracted 3 times with 25 ml of 0.5 M $NaHCO_3$, and the extracts were collected and acidified. The ether was next extracted 3 times with 25 ml of 0.5 M NaOH, and these extracts were also collected and acidified. The $NaHCO_3$ soluble material is the acidic fraction; the NaOH soluble material is the phenolic fraction; and the remaining ether soluble material is the neutral fraction.

Sample Preparation

Ether was removed from all samples by evaporation on a rotary evaporator. A vacuum pump was applied to the evaporator containing the samples for a minimum of 3 hours. The samples were then acidified and diluted to a known volume. To ensure reasonable sample recovery and to be certain the ether was removed, TOC and AOX mass balances were done around the fractionation scheme.

TOC Analysis

Measurement of TOC was done using a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate. Samples were prepared for TOC analysis by acidifying them, and sparging for 5 minutes with nitrogen to drive off any interfering carbonate species.

AOX Analysis

Measurement of AOX was done using a Dohrman model DX-20 organic halide analyzer. Sample preparation was done by a modification of method SCAN-W 9:89 (54). After the initial adsorption on carbon, the filtrate was treated with a second batch of carbon to minimize "breakthrough". All samples were shaken for an hour, the carbon filtered, the filtrate collected, and more carbon added to this filtrate. This filtrate was treated identically to the first AOX batch.

SUMMARY AND CONCLUSIONS

A 3 second D stage in the OD(EO) bleaching of a softwood kraft pulp, resulted in 67% of the delignification that occurred with the same sequence utilizing a 30 minute D stage. At the same time the overall whole effluent Cl/C_{100} was reduced to 34% of it's 30 minute value while the overall D + (EO) stage AOX was reduced to 26% of the 30 minute AOX. A one minute D stage achieved 84% of the delignification while generating only 42% of the AOX and 51% of the Cl/C_{100} of the 30 minute stage. Additional reaction time provided limited delignification benefits, while increasing quite significantly the level of chlorine substitution on dissolved organics. Based on effluent TOC measurements, the (EO) stage delignification remained constant for all D stage reaction times.

With the exception of the neutral fraction, the Cl/C_{100} of all effluent fractions were reduced to varying degrees as the D stage reaction time is shortened. In the environmentally significant ether soluble fraction, in addition to a sharp reduction in the Cl/C_{100}, the proportion of ether soluble material was reduced for short D stage reaction times and the proportion of ether soluble AOX (assumed to be "bad" AOX) reached a minimum under the 1 minute D stage conditions. These effects are likely to be caused primarily by the acidic fraction of the ether soluble material. In addition to reducing the overall effluent AOX, a bleaching sequence with a limited D stage may therefore represent environmental benefits in addition to the obvious reduction in total AOX.

ACKNOWLEDGMENTS

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Figure 1. Top View Schematic Diagram of D Stage Batch Bleaching Reactor.

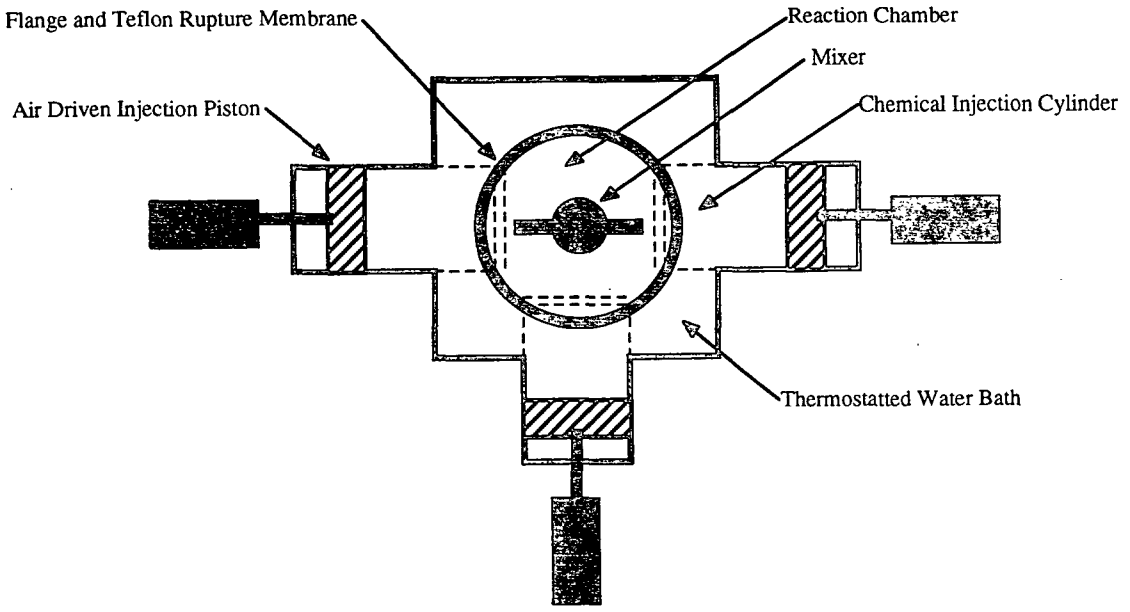
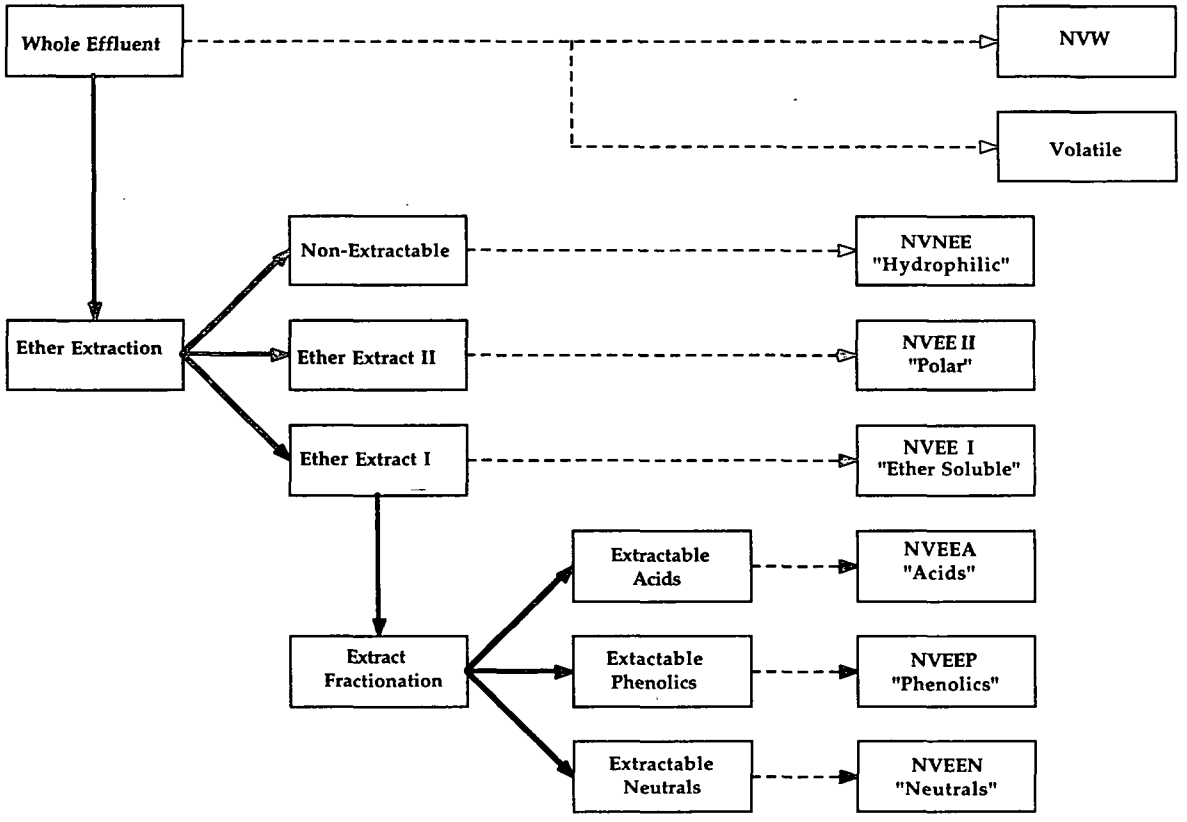


Figure 2. Effluent Fractionation.



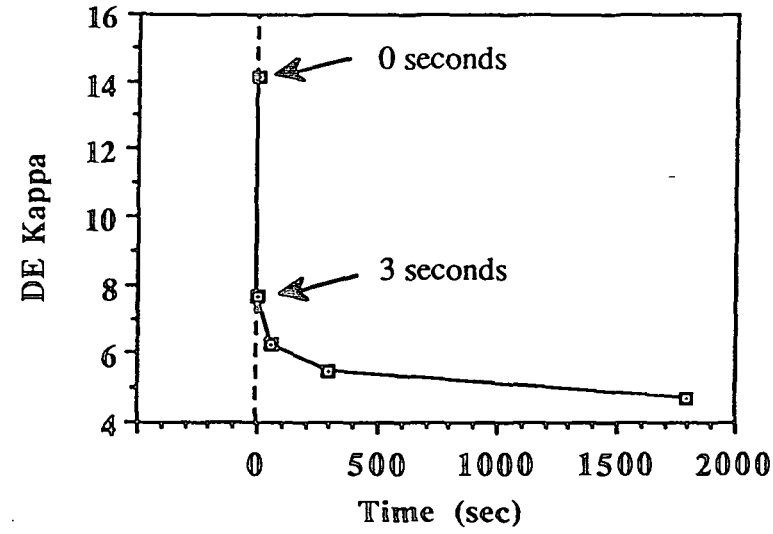


Figure 3. Pulp Delignification.

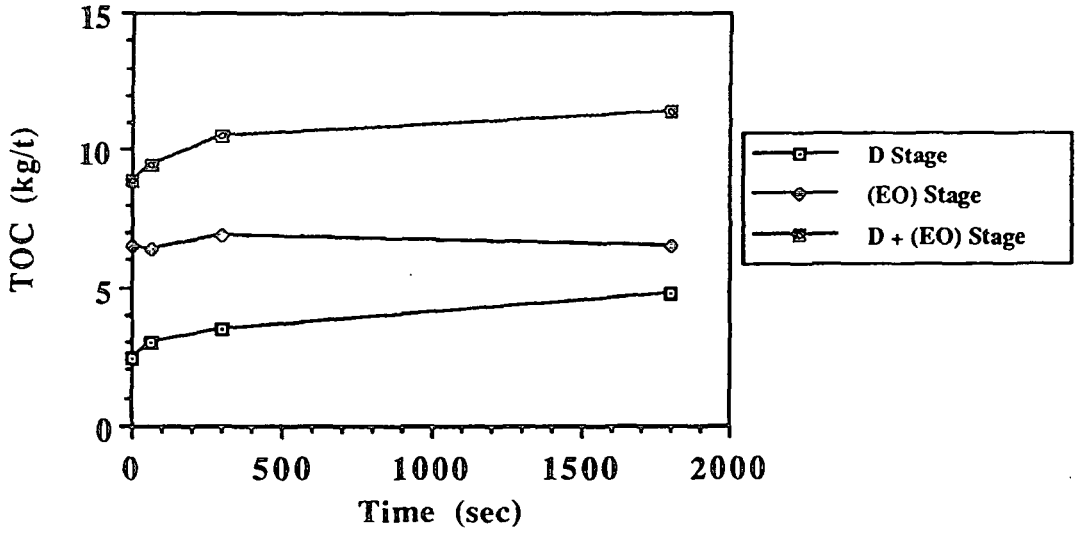


Figure 4. Whole Effluent TOC.

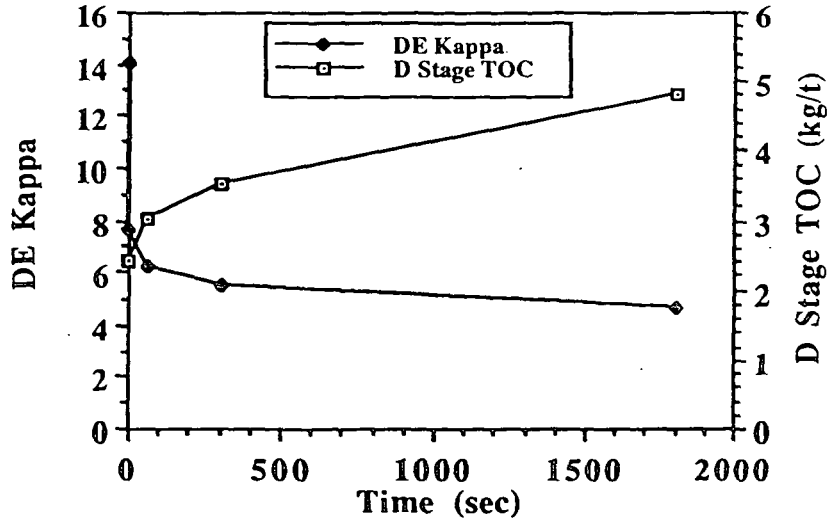


Figure 5. Kappa Numbers and D Stage TOC.

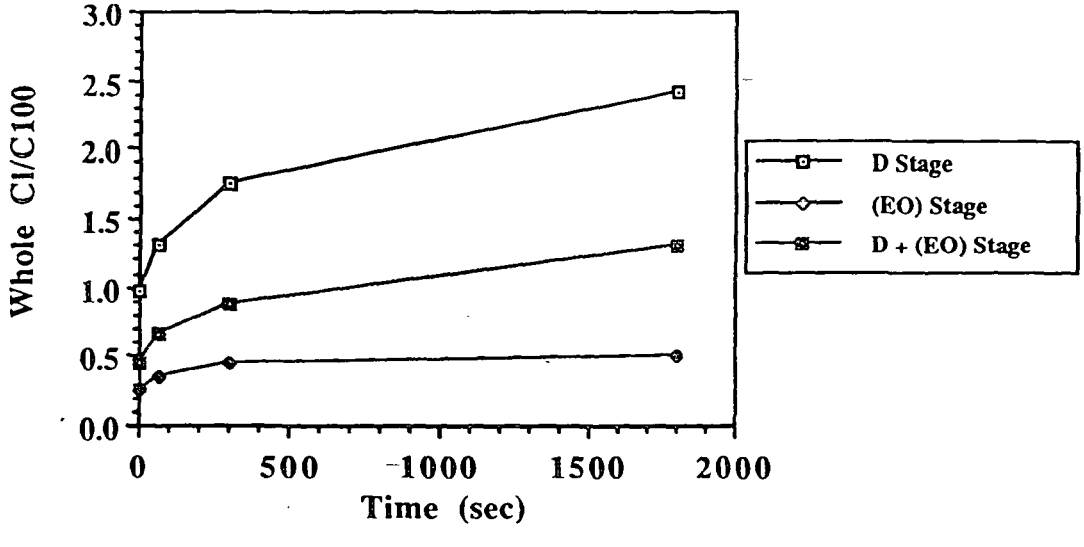


Figure 6. Whole Effluent Cl/C100.

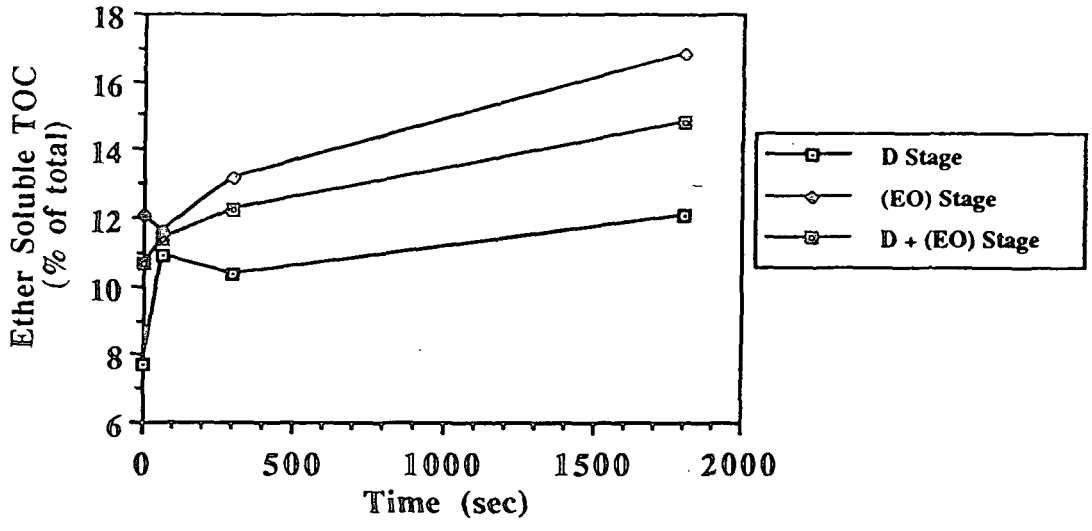


Figure 7. Ether Soluble TOC, as % of Total.

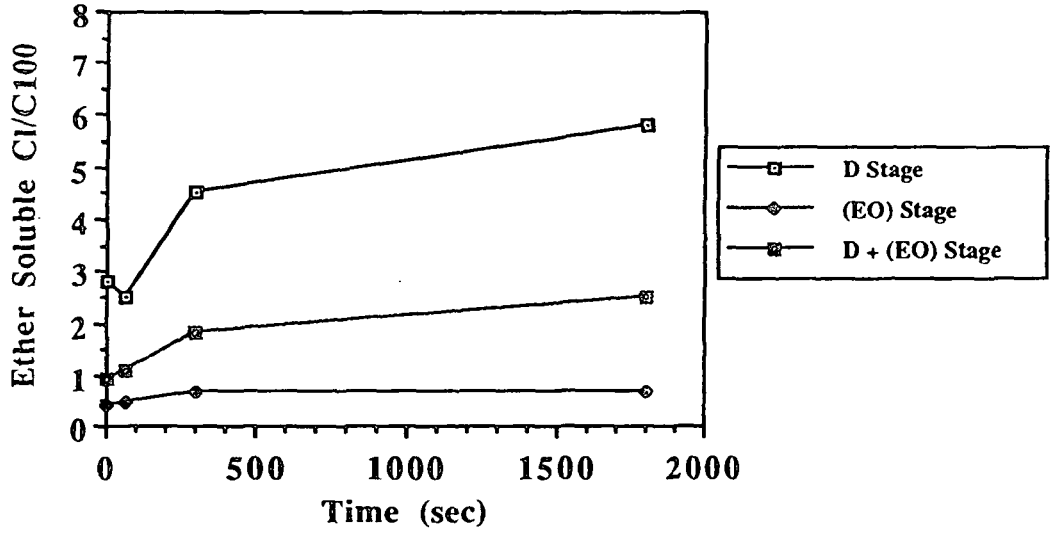


Figure 8. Ether Soluble Cl/C100.

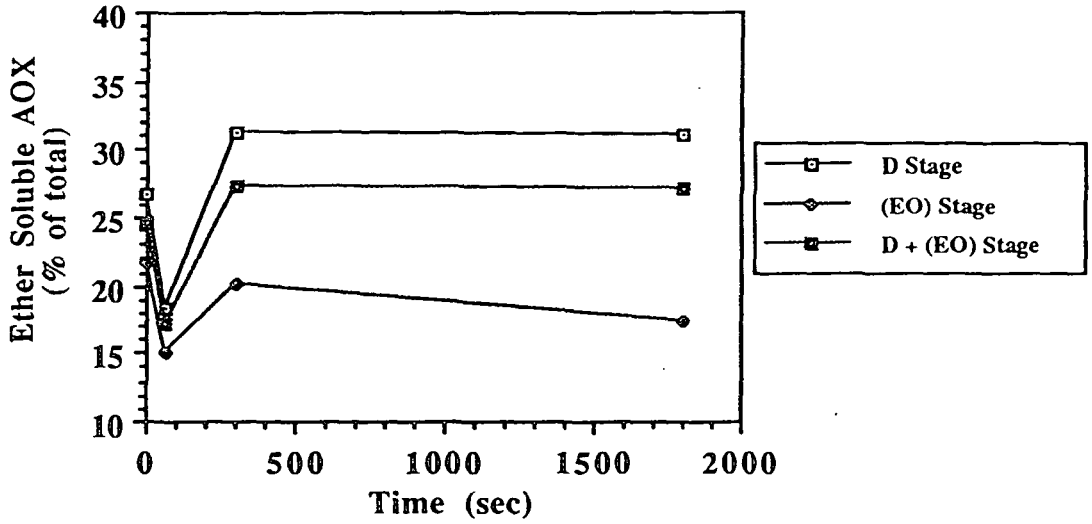


Figure 9. Ether Soluble AOX, as % of Total.

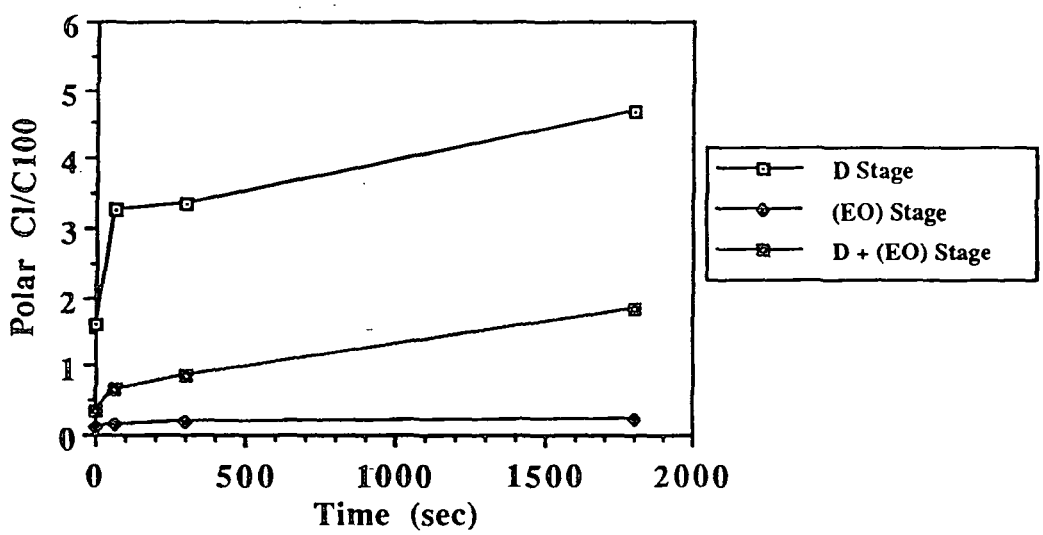


Figure 10. Polar Fraction Cl/C100.

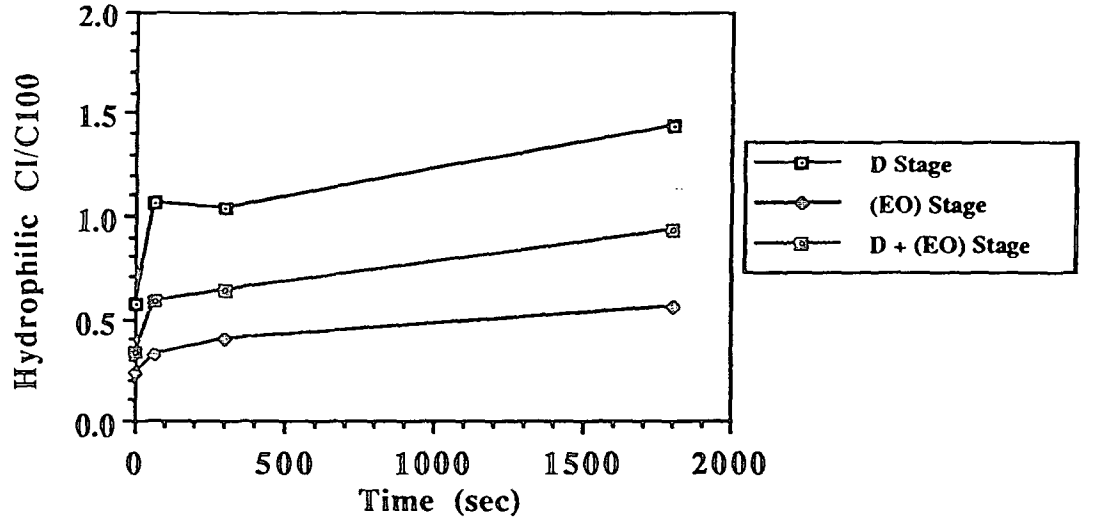


Figure 11. Hydrophilic Fraction Cl/C100.

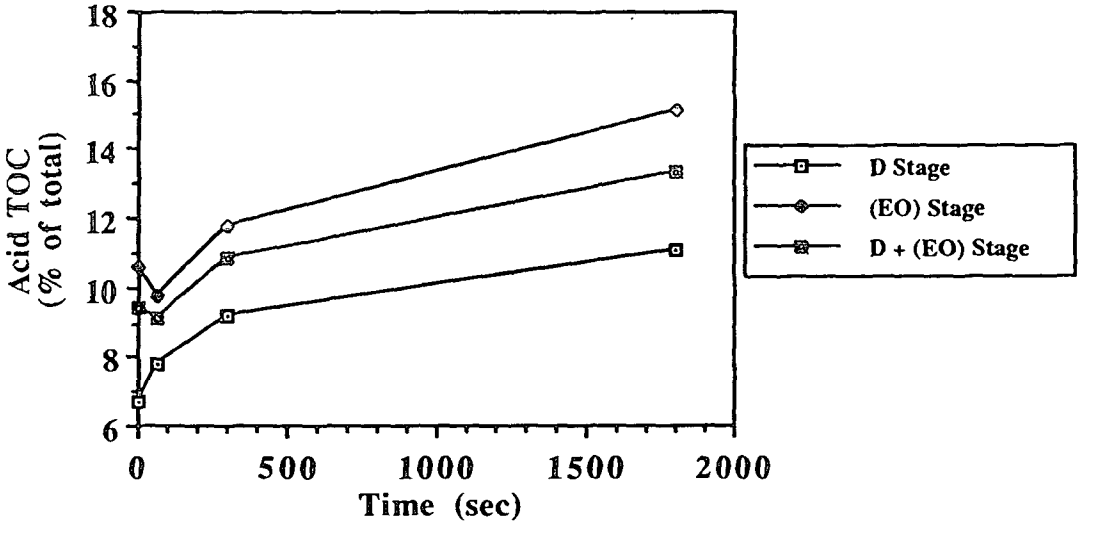


Figure 12. Acid Fraction TOC, as % of Total.

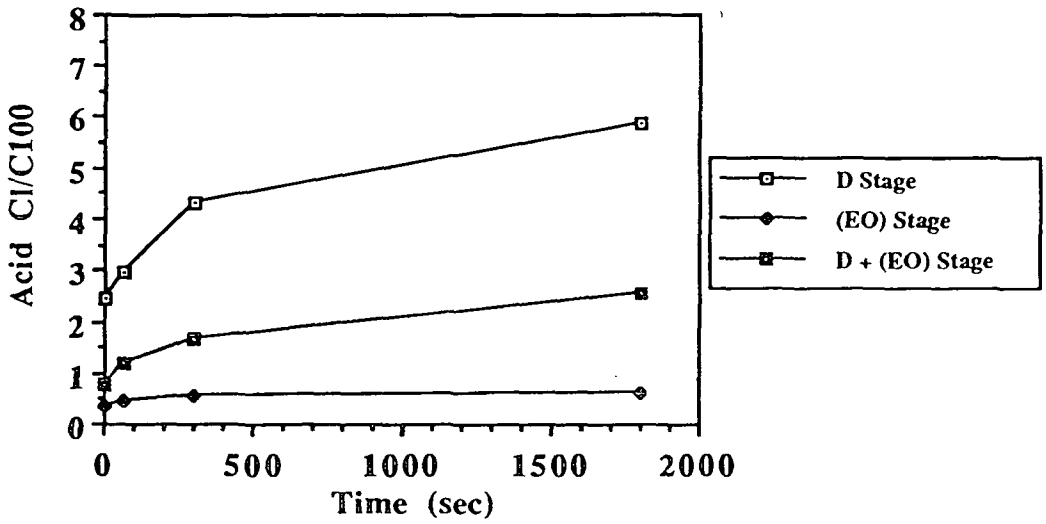


Figure 13. Acid Fraction Cl/C100.

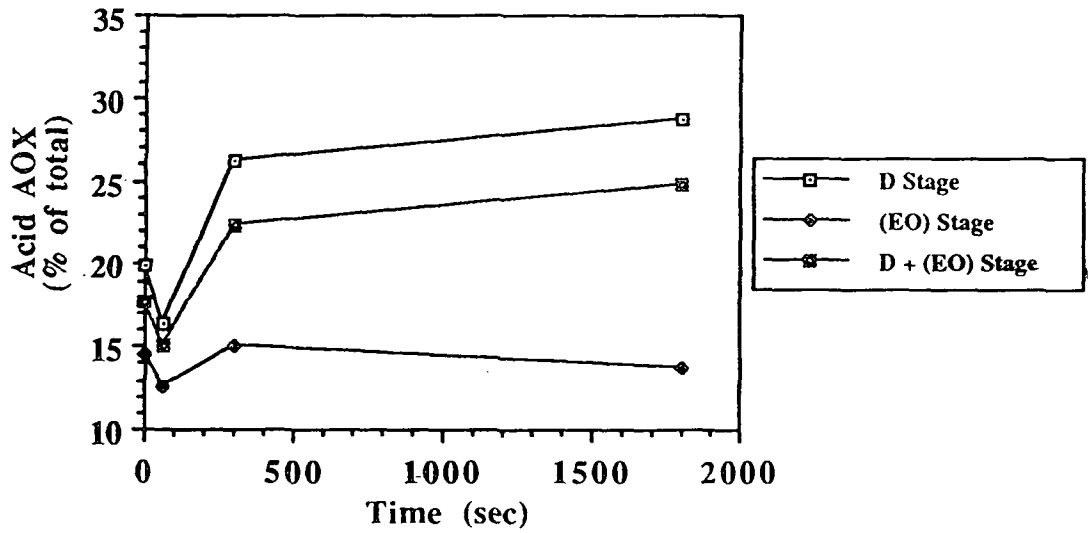


Figure 14. Acid Fraction AOX, as % of Total.

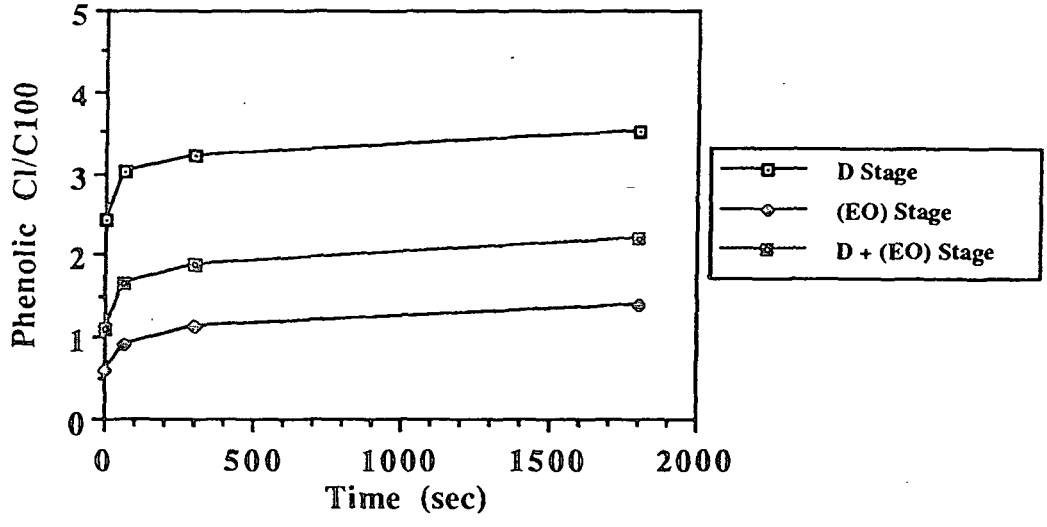


Figure 15. Phenolic Fraction Cl/C100.

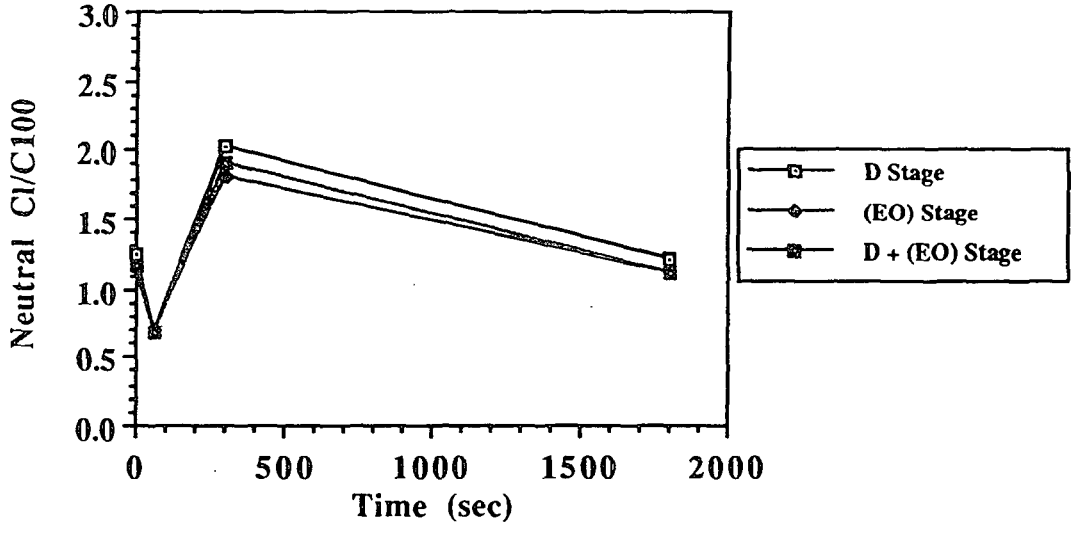


Figure 16. Neutral Fraction Cl/C100.

TABLE I. D + (EO) TOC AND KAPPA NUMBER DATA

D Stage Time, sec	D + (EO) TOC, kg/t	Kappa Number	Δ kappa	TOC/Δ kappa
3	8.56	8.23	5.87	1.46
	9.22	7.11	6.99	1.32
60	9.58	5.89	8.21	1.17
	9.31	6.56	7.54	1.23
300	10.50	5.17	8.93	1.18
	10.35	5.79	8.31	1.25
1800	11.25	4.37	9.73	1.16
	11.45	4.98	9.12	1.25

TABLE II. EFFLUENT FRACTION CODES AND DESCRIPTIONS OF FRACTIONS

Fraction Code	Description
NVW	Non-volatile, whole.
NVNEE	Non-volatile, non-ether extractable ("Hydrophilic").
NVEE II	Non-volatile, difficult to extract with ether ("Polar").
NVEE I	Non-volatile, readily ether extractable ("Ether Soluble").
NVEEA	Non-volatile, ether extractable acidic compounds ("Acids").
NVEEP	Non-volatile, ether extractable phenolic compounds ("Phenolics").
NVEEN	Non-volatile, ether extractable neutral compounds ("Neutrals").

TABLE III. WHOLE EFFLUENT AND SUMMED FRACTION CHARACTERISTICS

	D Stage Retention Time, sec			
D Stage	**3**	**60**	**300**	**1800**
TOC, kg/t	2.23 2.54	3.02 3.01	3.53 3.50	4.85 4.75
Total TOC[a], kg/t	2.45 3.03	3.13 3.14	3.42 3.74	4.84 4.95
AOX, kg/t	0.0706 0.0645	0.117 0.117	0.167 0.195	0.352 0.334
Total AOX[a], kg/t	0.0713 0.0573	0.133 0.128	0.149 0.167	0.361 0.299
Cl/C_{100}	1.07 0.86	1.31 1.31	1.61 1.88	2.46 2.38
(EO) Stage				
TOC, kg/t	6.33 6.68	6.56 6.30	6.97 6.85	6.40 6.70
Total TOC[a], kg/t	6.10 6.50	6.58 6.13	6.39 6.42	5.98 6.52
AOX, kg/t	0.0513 0.0427	0.0747 0.0614	0.0980 0.0856	0.0915 0.103
Total AOX[a], kg/t	0.0471 0.0440	0.0759 0.0667	0.0845 0.0779	0.106 0.127
Cl/C_{100}	0.27 0.22	0.39 0.33	0.48 0.42	0.48 0.52
D + (EO) Stages				
TOC, kg/t	8.56 9.22	9.58 9.31	10.5 10.4	11.3 11.5
Total TOC[a], kg/t	8.55 9.53	9.71 9.27	9.81 10.2	10.8 11.5
AOX, kg/t	0.122 0.107	0.192 0.178	0.265 0.281	0.444 0.437
Total AOX[a], kg/t	0.118 0.101	0.209 0.195	0.234 0.245	0.467 0.426
Cl/C_{100}	0.48 0.39	0.68 0.65	0.85 0.91	1.33 1.28

[a]Sum of corresponding values for volatile, hydrophilic, polar, acid, phenolic, and neutral fractions.

TABLE IV. ETHER SOLUBLE FRACTION

	D Stage Retention Time, sec			
D Stage	**3**	**60**	**300**	**1800**
TOC, kg/t	0.181 0.244	0.404 0.282	0.331 0.414	0.614 0.565
% of Total TOC	7.39 8.05	12.9 8.98	9.68 11.1	12.7 11.4
AOX, kg/t	0.0181 0.0160	0.0230 0.0250	0.0516 0.0466	0.0954 0.106
% of Total AOX	25.4 27.9	17.3 19.5	34.6 27.9	26.4 35.5
Cl/C_{100}	3.39 2.21	1.93 3.00	5.26 3.80	5.26 6.33
(EO) Stage				
TOC, kg/t	0.780 0.732	0.717 0.757	0.865 0.830	0.832 1.28
% of Total TOC	12.8 11.3	10.9 12.3	13.5 12.9	13.9 19.6
AOX, kg/t	0.0125 0.00739	0.0105 0.0108	0.0180 0.0149	0.0190 0.0217
% of Total AOX	26.5 16.8	13.8 16.2	21.3 19.1	17.9 17.1
Cl/C_{100}	0.54 0.34	0.50 0.48	0.70 0.61	0.78 0.58
D + (EO) Stages				
TOC, kg/t	0.961 0.976	1.12 1.04	1.20 1.24	1.45 1.85
% of Total TOC	11.2 10.2	11.5 11.2	12.2 12.2	13.4 16.1
AOX, kg/t	0.0306 0.0234	0.0335 0.0358	0.0696 0.0615	0.114 0.128
% of Total AOX	25.9 23.2	16.0 18.4	29.7 25.1	24.4 30.0
Cl/C_{100}	1.08 0.81	1.01 1.16	1.96 1.68	2.66 2.34

TABLE V. POLAR FRACTION

	D Stage Retention Time, sec			
D Stage	**3**	**60**	**300**	**1800**
TOC, kg/t	0.0917 0.153	0.116 0.139	0.182 0.191	0.256 0.336
% of Total TOC	3.74 5.05	3.71 4.43	5.32 5.11	5.29 6.79
AOX, kg/t	0.00622 0.00410	0.0150 0.00893	0.0193 0.0175	0.0375 0.0440
% of Total AOX	8.72 7.16	11.3 6.98	13.0 10.5	10.4 14.7
Cl/C_{100}	2.29 0.91	4.37 2.17	3.57 3.10	4.95 4.42
(EO) Stage				
TOC, kg/t	0.591 0.527	0.619 0.722	0.782 0.594	0.513 0.531
% of Total TOC	9.69 8.11	9.41 11.8	12.2 9.25	8.58 8.14
AOX, kg/t	0.00207 0.00168	0.00315 0.00282	0.00389 0.00344	0.00358 0.00335
% of Total AOX	4.39 3.82	4.15 4.23	4.60 4.42	3.91 2.64
Cl/C_{100}	0.12 0.11	0.17 0.13	0.17 0.20	0.24 0.21
D + (EO) Stages				
TOC, kg/t	0.683 0.680	0.735 0.861	0.964 0.785	0.769 0.867
% of Total TOC	7.98 7.14	7.57 9.29	9.83 7.70	7.12 7.54
AOX, kg/t	0.00829 0.00578	0.0182 0.0118	0.0232 0.0209	0.0411 0.0474
% of Total AOX	7.03 5.72	8.68 6.03	9.91 8.55	8.80 10.8
Cl/C_{100}	0.41 0.29	0.84 0.46	0.81 0.90	1.81 1.85

TABLE VI. HYDROPHILIC FRACTION

	D Stage Retention Time, sec			
D Stage	**3**	**60**	**300**	**1800**
TOC, kg/t	2.09 2.42	2.43 2.65	2.78 2.89	3.37 3.85
% of Total TOC	85.3 79.9	77.6 84.4	81.3 77.3	69.6 77.7
AOX, kg/t	0.0396 0.0352	0.0888 0.0687	0.0844 0.0903	0.149 0.156
% of Total AOX	55.5 54.6	66.8 53.7	56.6 54.1	41.3 52.2
Cl/C_{100}	0.64 0.49	1.24 0.88	1.03 1.05	1.50 1.37
(EO) Stage				
TOC, kg/t	4.28 5.06	5.03 4.71	4.69 4.97	4.62 4.71
% of Total TOC	70.2 77.8	76.4 76.8	73.4 77.4	77.3 72.2
AOX, kg/t	0.0304 0.0330	0.0522 0.0433	0.0531 0.0602	0.0810 0.0735
% of Total AOX	64.5 75.0	69.9 64.9	62.8 77.3	76.4 57.9
Cl/C_{100}	0.24 0.22	0.35 0.31	0.38 0.41	0.59 0.53
D + (EO) Stages				
TOC, kg/t	6.37 7.48	7.46 7.36	7.47 7.86	7.99 8.56
% of Total TOC	74.5 78.5	76.8 79.4	76.1 77.1	74.0 74.4
AOX, kg/t	0.0700 0.0682	0.141 0.112	0.138 0.151	0.230 0.230
% of Total AOX	59.3 67.5	67.5 57.4	58.8 61.4	49.3 53.9
Cl/C_{100}	0.37 0.31	0.64 0.51	0.62 0.65	0.97 0.91

TABLE VII. ACID FRACTION

D Stage	D Stage Retention Time, sec 3	60	300	1800
TOC, kg/t	0.150 0.219	0.232 0.255	0.278 0.381	0.547 0.533
% of Total TOC	6.12 7.22	7.41 8.12	8.13 10.2	11.3 10.8
AOX, kg/t	0.0137 0.0118	0.0193 0.0233	0.0397 0.0431	0.0953 0.0927
% of Total AOX	19.2 20.6	14.5 18.2	26.6 25.8	26.4 31.0
Cl/C_{100}	3.08 1.82	2.82 3.10	4.83 3.83	5.88 5.88
(EO) Stage				
TOC, kg/t	0.688 0.637	0.625 0.611	0.761 0.742	0.717 1.18
% of Total TOC	11.3 9.80	9.50 9.97	11.9 11.6	12.0 18.1
AOX, kg/t	0.00759 0.00570	0.00883 0.00899	0.0133 0.0113	0.0155 0.0165
% of Total AOX	16.1 13.0	11.6 13.5	15.7 14.5	14.6 13.0
Cl/C_{100}	0.37 0.30	0.48 0.50	0.59 0.52	0.73 0.47
D + (EO) Stages				
TOC, kg/t	0.838 0.856	0.857 0.866	1.04 1.12	1.26 1.71
% of Total TOC	9.80 8.98	8.83 9.34	10.6 11.0	11.7 14.9
AOX, kg/t	0.0213 0.0175	0.0281 0.0323	0.0530 0.0544	0.111 0.109
% of Total AOX	18.0 17.3	13.5 16.6	22.6 22.2	23.7 25.6
Cl/C_{100}	0.86 0.69	1.11 1.26	1.72 1.64	2.98 2.15

TABLE VIII. PHENOLIC FRACTION

	D Stage Retention Time, sec			
D Stage	**3**	**60**	**300**	**1800**
TOC, kg/t	0.0215 0.0189	0.0214 0.0284	0.0360 0.0240	0.0296 0.0343
% of Total TOC	0.878 0.624	0.684 0.904	1.05 0.642	0.612 0.693
AOX, kg/t	0.00163 0.00129	0.00193 0.00255	0.00334 0.00233	0.00330 0.00331
% of Total AOX	2.29 2.25	1.45 1.99	2.24 1.40	0.914 1.11
Cl/C_{100}	2.57 2.31	3.02 3.04	3.13 3.29	3.77 3.27
(EO) Stage				
TOC, kg/t	0.0507 0.0591	0.0428 0.0537	0.0592 0.0515	0.0442 0.0622
% of Total TOC	0.831 0.909	0.650 0.876	0.926 0.802	0.739 0.954
AOX, kg/t	0.000958 0.000953	0.00121 0.00139	0.00197 0.00181	0.00216 0.00213
% of Total AOX	2.03 2.17	1.59 2.08	2.33 2.32	2.04 1.68
Cl/C_{100}	0.64 0.55	0.96 0.87	1.12 1.18	1.65 1.15
D + (EO) Stages				
TOC, kg/t	0.0722 0.0780	0.0642 0.0821	0.0952 0.0755	0.0738 0.0965
% of Total TOC	0.844 0.818	0.661 0.886	0.970 0.740	0.683 0.839
AOX, kg/t	0.00259 0.00224	0.00314 0.00394	0.00531 0.00414	0.00546 0.00544
% of Total AOX	2.19 2.22	1.50 2.02	2.27 1.69	1.17 1.28
Cl/C_{100}	1.21 0.97	1.65 1.62	1.89 1.85	2.50 1.91

TABLE IX. NEUTRAL FRACTION

D Stage	D Stage Retention Time, sec 3	60	300	1800
TOC, kg/t	0.0495 0.0286	0.151[a] 0.0524	0.0551 0.0337	0.159 0.0538
% of Total TOC	2.02 0.944	4.82[a] 1.67	1.61 0.901	3.29 1.13
AOX, kg/t	0.00131 0.00135	0.00179[a] 0.00150	0.00265 0.00240	0.00301 0.00282
% of Total AOX	1.84 2.36	1.35[a] 1.17	1.78 1.44	0.834 0.943
Cl/C_{100}	0.89 1.59	0.40[a] 0.96	1.62 2.41	0.64 1.77
(EO) Stage				
TOC, kg/t	0.0238 0.0241	0.0566 0.0296	0.0486 0.0160	0.0267 0.0378[a]
% of Total TOC	0.390 0.371	0.860 0.483	0.761 0.249	0.446 0.580[a]
AOX, kg/t	0.000996 0.000614	0.000618 0.000908	0.00169 0.00115	0.000856 0.00135
% of Total AOX	2.11 1.40	0.927 1.36	2.00 1.48	0.808 1.06
Cl/C_{100}	1.41 0.86	0.37 1.04	1.18 2.43	1.09 1.15[a]
D + (EO) Stages				
TOC, kg/t	0.0733 0.0527	0.208 0.082	0.104 0.0497	0.186 0.0916
% of Total TOC	0.857 0.553	2.14 0.885	1.06 0.487	1.72 0.797
AOX, kg/t	0.00231 0.00196	0.00241 0.00241	0.00434 0.00355	0.00387 0.00417
% of Total AOX	1.95 1.94	1.15 1.23	1.85 1.45	0.828 0.979
Cl/C_{100}	1.07 1.26	0.39 0.99	1.41 2.41	0.70 1.54

[a]Calculated using AOX and/or TOC balances.

TABLE X. VOLATILE FRACTION

	D Stage Retention Time, sec			
D Stage	**3**	**60**	**300**	**1800**
TOC, kg/t	0.0920 0.190	0.178 0.0192	0.0898 0.216	0.475 0.139
% of Total TOC	3.76 6.27	5.69 0.611	2.63 5.78	9.81 2.81
AOX, kg/t	0.00880 0.00356	0.00756 0.0229	n.d. 0.0116	0.0724 n.d.
% of Total AOX	12.3 6.21	5.68 17.9	n.d. 6.95	20.1 n.d.
Cl/C_{100}	3.24 0.63	1.44 40.3	n.d. 1.82	5.15 n.d.
(EO) Stage				
TOC, kg/t	0.466 0.191	0.205 n.d.	0.0457 0.0456	0.0546 n.d.
% of Total TOC	7.64 2.94	3.12 n.d.	0.715 0.710	0.913 n.d.
AOX, kg/t	0.00508 0.00205	0.00986 0.00931	0.0105 n.d.	0.00311 0.000135
% of Total AOX	10.8 4.66	13.0 14.0	12.4 n.d.	2.93 0.106
Cl/C_{100}	0.37 0.36	1.62 n.d.	7.81 n.d.	1.92 n.d.
D + (EO) Stages				
TOC, kg/t	0.558 0.381	0.383 n.d.	0.136 0.262	0.530 n.d.
% of Total TOC	6.53 4.00	3.94 n.d.	1.38 2.56	4.90 n.d.
AOX, kg/t	0.0139 0.00561	0.0174 0.0322	n.d. n.d.	0.0755 n.d.
% of Total AOX	11.8 5.55	8.33 16.5	n.d. n.d.	16.2 n.d.
Cl/C_{100}	0.84 0.50	1.54 n.d.	n.d. n.d.	4.82 n.d.

n.d. - Not determined, due to no difference between whole and non-volatile whole effluent samples.

Section 5 Conclusions

Effluents from the OD(EO) partial bleaching sequence, using different duration D stages (3 seconds to 30 minutes), were compared using the ether extraction based effluent fractionation.

The OD(EO) bleaching sequence utilizing short duration D stages (one minute or less) had 3 advantages from an environmental point of view. The sequence using a short duration D stage produced a smaller proportion of material within the environmentally significant ether soluble fraction. In addition, that material was substituted by chlorine atoms to a reduced extent. Also with a 1 minute duration D stage, the proportion of ether soluble AOX (presumed to be "bad" AOX) reached a sharp minimum. These effects were most likely caused by the acidic subfraction of the ether soluble material, since the same trends in the data were observed there.

Short reaction times, in addition to providing possible environmental benefits, provided up to 85% of the delignification that occurred at extended times. At these same short reaction times, only 40% of the overall AOX was formed. Since the level of AOX at short D stage reaction times was near that of proposed AOX limits, the OD(EO) sequence with a short duration D stage may allow compliance.

GEL PERMEATION CHROMATOGRAPHY

This portion of the Results and Discussion consists of 2 sections. Both sections (Sections 6 and 7) consider gel permeation chromatography (GPC) for determination of the molecular weight distributions of pulp bleaching effluents. Section 6 discusses the development of a GPC method, and Section 7 reports the results of the application of the GPC method to bleaching effluents.

Section 6: Development of a Method of Aqueous Gel Permeation Chromatography for the Determination of Molecular Weight Distributions of Bleaching Effluents

In Section 6, a compilation of the preliminary gel permeation chromatography (GPC) work is presented. This preliminary work led to the development of the GPC method that was used to determine the molecular weight distributions of the effluents.

The GPC method utilized 2 Sephadex gel columns in series, 0.1 N LiCl eluent, and total organic carbon (TOC) detection. The method had several significant advantages over other GPC methods which allowed it to provide more accurate molecular weight distributions for bleaching effluents. These advantages included increased low molecular weight resolution, elimination of association, and a universal detection system capable of equally determining both lignin and carbohydrate fragments.

DEVELOPMENT OF A METHOD OF AQUEOUS GEL PERMEATION CHROMATOGRAPHY FOR THE DETERMINATION OF MOLECULAR WEIGHT DISTRIBUTIONS OF BLEACHING EFFLUENTS

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ABSTRACT

A method of aqueous gel permeation chromatography (GPC) was developed and used to determine the molecular weight distributions of bleach plant effluents and ether extracts of the effluents. The method employs two Sephadex G columns in series, elution by 0.1 M LiCl and detection by total organic carbon (TOC) analysis of eluent fractions. Initially, a single column and ultraviolet (UV) detection were used. Subsequent experiments showed that the dual column system gave better separation at low molecular weights. Alkaline eluents, such as NaOH and $NaHCO_3$, caused changes in the apparent molecular weight distributions of acidic stage bleaching effluents, and were therefore considered inappropriate.

The GPC system was calibrated using polyethylene glycols of known molecular weight, and the distributions of several samples determined. The molecular weight distributions of bleaching effluents determined by this method were much lower than those reported for ultrafiltration. The entire (C+D) effluent and over 70% of the E_1 effluent were eluted at relative retention volumes corresponding to molecular weights of less than 1000. The ether extracts of both (C+D) and E_1 stage effluents had distributions that did not exceed 1000.

The method is well suited to bleaching effluents which are comprised mostly of hydrophilic materials. Incomplete recovery was observed only for the most non-polar solutes, found in the ether soluble fraction. This is not serious because the ether extract is a relatively small fraction and is known to contain only low molecular weight components. TOC determination was used for detection because, unlike UV, it is not biased toward strongly UV absorbing solutes. An additional advantage of a universal detection method such as TOC is that it enables determination of the degree to which the sample components are completely recovered from the columns.

INTRODUCTION

Molecular weight distributions of components of the waste streams of pulp manufacture have been determined by ultrafiltration and gel permeation (or size exclusion) chromatography. Ultrafiltration is a method in which solutions of dissolved polymeric materials are filtered under pressure, using membranes with known pore sizes. Small molecules pass through the pores while larger molecules are retained. By using, in succession, a series of such filters, beginning with one that retains only very large molecules and ending with one that only small molecules can pass through, a distribution of molecular size may be found. Ultrafiltration has been used to fractionate kraft black liquor (1, 2). It has also been applied to pulp bleaching effluents for the determination of molecular weight distributions (3-7). Because of possible aggregation and dilution effects, ultrafiltration may give incorrect distributions (8).

Gel permeation chromatography (GPC) is another commonly used method for the determination of molecular weight distributions of solutions of polymeric materials. In GPC, solutions of polymers are separated by molecular size on columns of porous gel material. The gel particles contain pores with a wide distribution of sizes. Large molecules can enter few of the pores, and are eluted first since less of the column volume is available to them. More of the total column volume is available to smaller molecules since they can penetrate more pores in the gel. Small molecules are therefore retained longer in the gel and are eluted later. GPC has been used in the determination of molecular weight distributions for carbohydrates and cellulosics (9-11), lignin model compounds (12, 13), and lignin material from various pulping and bleaching processes (1, 2, 8, 9, 10, 13, 14-24).

Certain factors exist that may lead to elution of polymers not entirely according to molecular size (25). Among these are ion exclusion, ion inclusion, intramolecular electrostatic effects, and adsorption. Most ionic effects can be controlled by increasing the ionic strength of the eluent (25). Another phenomenon observed in GPC of lignins is the formation of association complexes between lignin molecules (14-16). Evidence of association is the occurrence of bimodal molecular weight distribution curves (15, 16). The dis-

appearance of the bimodality is evidence that association has been eliminated. Commonly used systems that are free of association are Sephadex LH-type gels with 0.1 M LiCl dissolved in DMF as the eluent (16, 19) and Sephadex G-type gels with aqueous NaOH as the eluent (17, 19, 20, 22, 24). Incorporation of the salts in the eluents is believed to cause disruption of association in lignin and lignin-like molecules. Evidence for this is the shift in the distribution toward lower molecular weight and away from bimodality as salt concentration is increased (16, 19).

In the present study, a GPC method for determining molecular weight distributions of bleaching effluent components is considered. This method eliminates the problem of association, has increased resolution, causes minimal time dependent changes in the distributions of acid stage bleaching effluents, and uses a means of detection that is unbiased by the chemical structure of the material. The development of the method is described here and molecular weight distributions for both bleaching effluents and their ether extracts are presented.

EXPERIMENTAL APPROACH

The majority of the experiments were done using mill produced (C+D) and E_1 stage effluents. Polyethylene glycols, sulfonated polystyrenes, and various low molecular weight compounds were used as standards. The results reported here will focus on the distributions of effluent components under different GPC conditions. Calibration of the GPC system is considered in detail only with regard to the final system. Enough eluent solute was added to all standards and effluent solutions to adjust the concentration of these solutions to that of the original eluent.

Various GPC conditions were investigated: single columns, columns in series, different eluent systems, and different eluent flow rates. The retention time of a given solute (or equivalently, the volume of eluent required to elute it) is inversely related to its molecular size, but also depends on the conditions of the separation. In particular, eluent pH changes will result in altered retention time due to gel shrinkage and swelling.

To account for differences in retention under different operating conditions, all gel permeation chromatograms were normalized to relative retention volume scales. The scales were based on the retention of a high molecular weight compound that is completely excluded from pores in the gel, and a low molecular weight compound that is, in theory, completely included in all pores. Relative retention volume is calculated as follows:

$$\text{Relative Retention Volume} = R_s - R_h \,/\, R_l - R_h$$

where

R_s = retention volume of sample.

R_l = retention volume of low molecular weight standard.

R_h = retention volume of high molecular weight standard.

The high molecular weight standard corresponds to a relative retention volume of 0.0 on this scale, and the low molecular weight standard to a value of 1.0. Two different low molecular weight materials were used to estimate R_l: dimethoxybenzoic acid was used when detection was by UV absorbance, and methanol was used when detection was by total organic carbon (TOC) determination. The dimethoxybenzoic acid was not eluted solely on a molecular weight basis, as will be shown later, and was therefore a poor choice. The same retention scale was used within each set of experiments, so comparisons within each set are valid. However, the two relative retention volume scales are not directly comparable. Only in the final experiments, in which detection was by TOC analysis, do molecular weight values correspond directly to the relative retention volume scale.

RESULTS AND DISCUSSION

The objective of the experiments was to develop a method of gel permeation chromatography that was applicable to the determination of molecular weight distributions for pulp bleaching effluents. An ideal method should give accurate molecular weight distributions which are not altered by adsorption to the gel or by associative effects. It should also have good resolution and be reproducible.

The starting point for method development was the work of Sagfors and Starck (22), who used Sephadex G-50 gel and eluted bleaching effluent components from the column with 0.5 M NaOH. Systems of this type have been commonly used in determinations of molecular weight distributions of alkaline pulping waste (17, 19, 20), and molecular association was shown to be negligible (17).

Single Column GPC

In the early stage of the work, a single column containing Sephadex G-50 gel was used, and solutes were eluted with 0.5 M NaOH and detected by UV absorbance at 280 nm. The resulting GPC chromatograms for (C+D) and E_1 stage effluents are shown in Figures 1 and 2. These distributions are very similar to those obtained by Sagfors and Starck.

Concerns about the possibility of causing chemical changes in acid stage bleaching effluents by elution with alkaline systems, led to a consideration of other eluents. Elution with water gave single large peaks at the retention volume of the high molecular weight standard, indicating associative effects. A 0.1 M aqueous LiCl eluent gave similar distributions to those obtained with 0.5 M NaOH (Figures 1 and 2), indicating that LiCl broke the previously observed associations. To increase the UV absorbance of the effluents, $NaHCO_3$ was added to the LiCl eluent, and the distributions were again obtained (Figures 1 and 2). They are similar to the ones obtained using the other eluents. Although some differences may be seen, few distinguishing characteristics exist. This is not surprising since the G-50 gel only has the ability to separate compounds with molecular weights above 1,500.

Dual Column GPC

To increase resolution, particularly at low molecular weights, 2 columns were used in series. The first was packed with Sephadex G-50, as before, and the second was packed with Sephadex G-15. The G-50 gel has the capability to separate solutes having molecular weights of 30,000 to 1,500, and the G-15 gel has separation capability below 1,500. By connecting the columns in series, those compounds not resolved by the first column are separated by the second, and those separated by the first column pass unchanged through the second.

Distributions for the effluents were obtained using the dual column system, with the same 3 eluents studied with the single column. The distributions for the (C+D) effluent are shown in Figure 3 and those for the E_1 effluent are shown in Figure 4. Based on the (C+D) effluent distributions, it is clear that the 2 column system gives increased separation at the low molecular weight end of the distributions. The (C+D) effluent distributions from the 3 sets of conditions are easily distinguishable from one another. The E_1 stage distributions also gain distinguishing features at low molecular weights.

Different eluents gave widely varying distributions for the (C+D) stage effluents, as shown by Figure 3. It was unclear which, if any, of the distributions were correct. During the course of these experiments it was discovered that the distributions obtained with the 0.1 M LiCl/0.1 M $NaHCO_3$ eluent changed as the (C+D) effluent was contacted with the eluent solutes for different lengths of time. A sample of the (C+D) stage effluent was adjusted to 0.1 molarity in both $NaHCO_3$ and LiCl and the sample distribution was determined immediately after sample preparation, several days after sample preparation, and again several weeks later. The results are shown in Figure 5. The distribution shifted toward higher apparent molecular weights as exposure time to the eluent solutes increased. In fact, after an extended exposure time, the distribution became similar in appearance to that obtained using the 0.5 M NaOH (Figure 6). These effects may be due to associative behavior. Although alkaline solutions can eliminate associative behavior, incubation in alkaline solutions can also allow association to occur (15). Similar associative behavior of the (C+D) stage bleaching effluent may occur in solutions of both 0.5 M NaOH and 0.1 M LiCl/0.1 M $NaHCO_3$. However, in the bicarbonate case, the association process may be slow enough to be observed by a sequence of distributions determined after different exposure times. The use of alkaline eluents for the determination of molecular weight distributions of (C+D) or other acidic stage bleaching effluents is clearly unsatisfactory.

GPC With TOC Detection

All previous distributions had been obtained by using a flow-through UV absorbance detector. UV detection is dependent on chemical structure of the solute, and biases distributions toward highly absorbing materials. An alternative is TOC analysis. TOC measures the amount of organic carbon, unbiased by chemical structure.

In this group of experiments, the relative retention volume scale was based on a high molecular weight polyethylene glycol and methanol. The relative retention volume for a series of polyethylene glycol (PEG) standards and methanol are given in Table I. Samples were collected as they emerged from the columns, and each sample was individually analyzed for TOC.

The first experiment was a determination of (C+D) effluent stability to the 0.1 M LiCl eluent. The (C+D) effluent was prepared, run immediately, then run again after 9 days. Although the two distributions are not identical (Figure 7), they are very similar, and are much more reproducible than when alkaline eluents were used.

The (C+D) and E_1 effluents were analyzed by this system and the distributions are shown in Figure 8. Cumulative molecular weight distributions for the effluents are shown in Figure 9. Each point in the cumulative distribution shows the percentage of effluent TOC corresponding to a molecular weight less than the given molecular weight. As expected, the (C+D) effluent contains a greater percentage of low molecular weight components. The entire (C+D) effluent consists of material with an apparent molecular weight of less than 1000. About 70% of the E_1 effluent is eluted at a relative retention volume corresponding to a molecular weight less than 1000. In fact the peak that occurs in the E_1 stage distribution, between relative retention values of 0.7 and 0.9, corresponds to material with molecular weights of less than 300. This is contrary to earlier results obtained by ultrafiltration in which far more high molecular weight material was found (3-7). The latter result may be explained in terms of concentration dependent clogging of membranes which inhibits the passage of low molecular weight material (8).

It is interesting to compare the E_1 effluent distribution obtained by UV absorption with that obtained by TOC analysis. Such a comparison (Figure 4 compared to Figure 8) indicates that the high molecular weight E_1 stage material absorbs UV strongly while the lower molecular weight material absorbs very little. Similar arguments may be made for the (C+D) stage effluent distributions.

Ether extracts of bleaching effluents have been isolated and characterized because the majority of compounds of environmental interest are ether soluble (26). Ether extracts of both effluents were prepared, dissolved in water, the ether removed, and the molecular weight distributions determined. These distributions are shown in Figure 10. The ether extractable effluent material is apparently of low molecular weight (almost entirely less than 300), as expected on the basis of earlier work, which showed the number average molecular weight of ether extracts to be less than 300 (27).

Characterization of the Dual Column System

A variety of standards were run and a calibration curve made for the dual column system. Polyethylene glycol (PEG) standards covering a wide range of molecular weights (106-19,700) were used as standards when TOC was the means of detection. Since material in bleaching effluents has been shown to be largely aliphatic and highly oxidized (3, 4), PEG should be a reasonable model of residual lignin after bleaching. Sulfonated polystyrene standards (SPS), which were used during the UV detection experiments, and a variety of low molecular weight acids were also run to calibrate this system. The calibration curve is shown in Figure 11. Surprisingly the PEG and SPS standards fall on the same curve even though they differ greatly in structure. Several acids known to exist in effluents (acetic, chloroacetic, oxalic, malonic, and succinic acids) and others of a similar type (muconic and adipic acids) fall on or very near the curve. Others (azelaic acid and dimethoxybenzoic acid) are far from the curve.

It is clear from these results, that dimethoxybenzoic acid was a poor choice for a low molecular weight standard in the early experiments, since it does not elute solely on the basis of molecular size. Its elution behavior is determined by a combination of molecular size and attraction to the gel. The compounds which fall far from the calibration curve were quite water insoluble, and were therefore more non-polar and more likely to adsorb to the gel column than the more water soluble species. Highly polar, highly water soluble molecules move through the column and are separated on the basis of molecular size, while non-polar, water insoluble compounds are adsorbed to varying extents on the gel and are eluted at longer than expected times, or in extreme cases not eluted at all.

Further support for this theory is provided by the recovery of TOC after fractionation by GPC. An advantage of TOC detection is that it allows a measurement of TOC recovery from the columns after fractionation. If no adsorption to the column occurs, the sum of TOC in all fractions should equal that of the initial effluent sample before fractionation. The ether extractable effluent material, which is the most non-polar effluent fraction and the most water insoluble fraction (distributions seen in Figure 10), had TOC recoveries of only 42 and 66% for the (C+D) and E_1 effluents, while recoveries for the effluent components not extracted by ether were 100% or greater. Any recovery greater than 100% may have been the result of ad-

sorbed material removal by additional elution. Because of solute losses and the resulting contamination of the columns, this system is not well suited to the ether extracts. The GPC method using Sephadex gels and 0.1 M aqueous LiCl eluent is most valid for polar materials, for example non-ether extractable effluent fractions, or effluents from ClO_2, oxygen, or ozone bleaching.

Due to adsorption effects, the whole effluent distributions (Figure 9) may be altered somewhat. However, since the amount of the ether extractable TOC is generally 10% or less of the total TOC (26), the effect should be small. Since any adsorbed material is likely to be ether extractable and therefore of low molecular weight, the low molecular weight end of the distributions are probably affected most.

EXPERIMENTAL METHODS

Sample Preparation

Bleaching effluents were mill produced, and ether extracts were collected as discussed elsewhere (26). Eluent solutes were added to all samples to adjust them to the same concentration as the eluents. The sample pH was also adjusted to the pH of the eluent system. When TOC detection was implemented, samples were acidified to pH 2, the samples sparged with nitrogen to eliminate carbonate, and the sample pH adjusted upward to that of the LiCl eluent (pH 5.0-5.5).

Gel Preparation and Column Packing

Sephadex G-type gels, made of crosslinked dextran, were used for GPC work. The gels were purchased in a powdered state, were swelled first in water and then in the eluent system, before column packing. Pharmacia HR 16/50 columns were used for GPC work, and a HR 16 column packing reservoir used during the packing process. Each column was packed individually. The swelled gel was added to the column and the packing reservoir and the gel was packed into the column using flow rates and pressures in excess of those used during chromatography experiments. At least 2 column volumes of eluent (200 ml) was passed through the columns under these conditions to stabilize the gel bed. Once the bed was stable, the column top adapter was attached and the columns were used.

Gel Permeation Chromatography

Chromatography and column packing were done using a Varian Model 5000 HPLC. When UV detection was used, the flow from the columns passed directly into the UV detector associated with the instrument. When TOC detection was used, 100 separate 3 ml samples were collected in a fraction collector, and the TOC determined for each. Flow rates of 0.5 ml/min were used in the UV detection studies, while 1 ml/min flow rates were used for TOC detection experiments.

TOC Analysis

Measurement of TOC was done using a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate.

SUMMARY AND CONCLUSIONS

A method of aqueous gel permeation chromatography has been developed and applied to mill produced bleaching effluents and ether extracts of the effluents. The method uses 2 Sephadex G-type gel columns in series - one to separate high molecular weight material and the other to separate materials of low molecular weight. The eluent system is 0.1 M LiCl, and detection is done by total organic carbon analysis. The dual column system gives improved low molecular weight separation compared to a single column system, and 0.1 M LiCl does not cause changes in the distributions of acidic stage effluents as alkaline eluent systems do. TOC analysis provides detection that is unbiased by the chemical structures of eluted material, unlike UV detection.

The method was found to be most appropriately used for hydrophilic materials, since such materials have minimal interaction with the column. In the present study the method was used to estimate the molecular weight distribution for bleaching effluents and ether extracts of effluents, although the system is not ideally suited to ether extracts. The effluent distributions were of a much lower molecular weight than those reported for ultrafiltration. All (C+D) effluent components had molecular weights of less than 1000, as did about 70% of the E_1 stage effluent. The ether extracts from both stages were entirely below 1000.

ACKNOWLEDGMENTS

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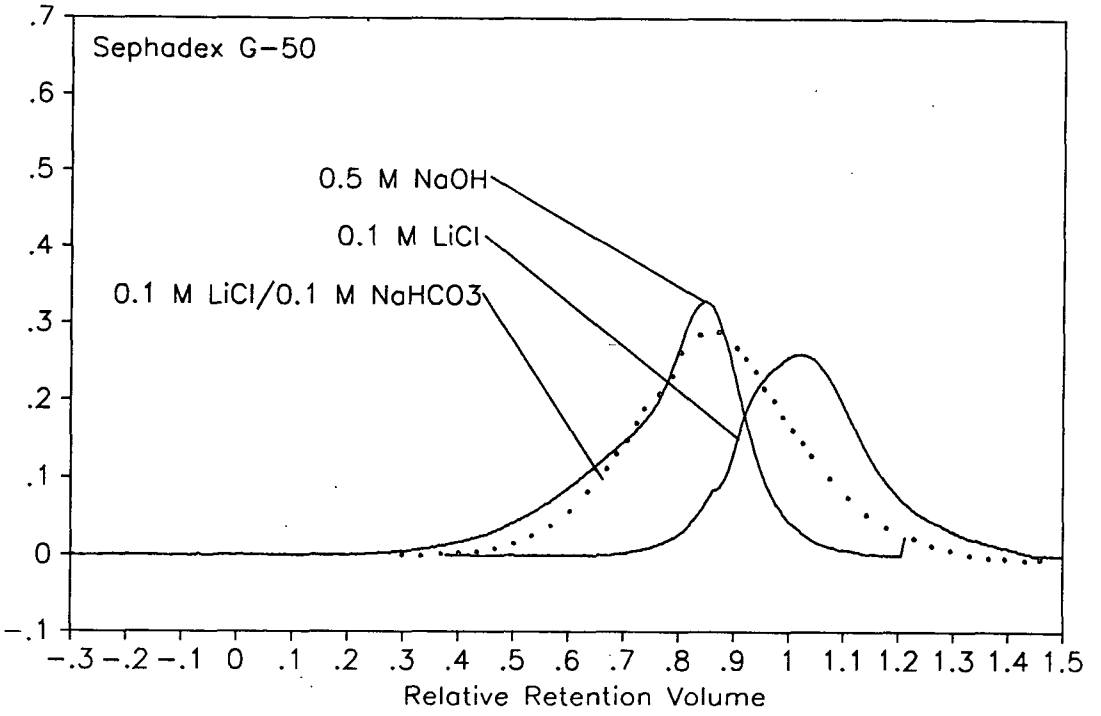

Figure 1. Single Column GPC of (C+D) Stage Effluent.

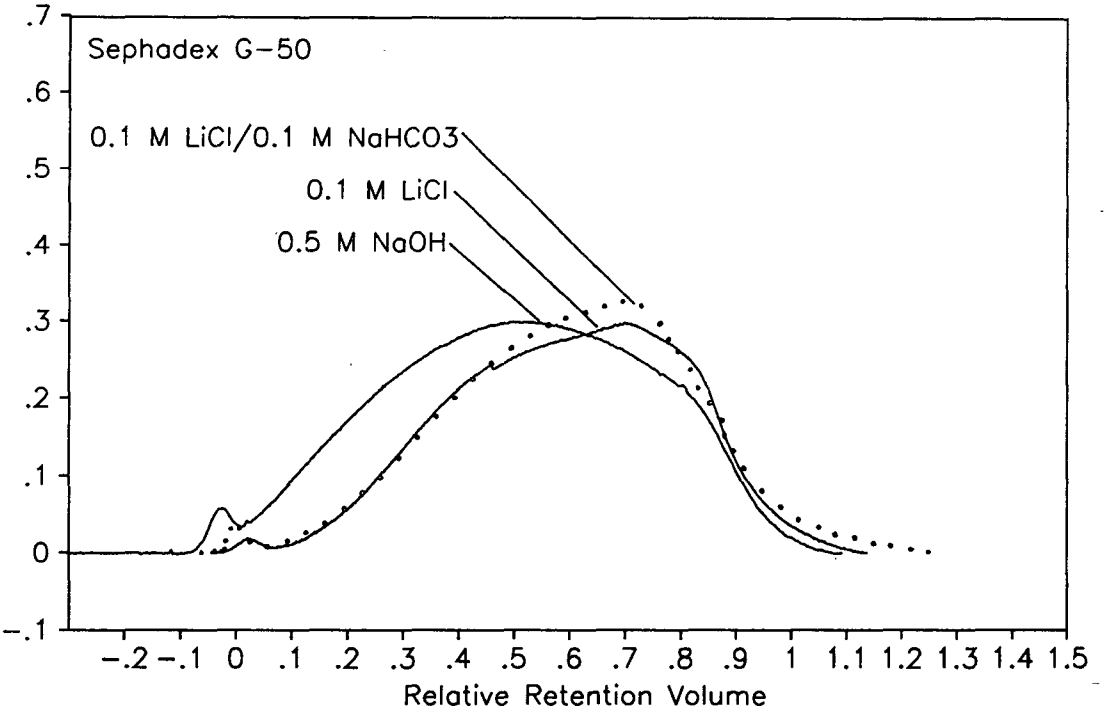

Figure 2. Single Column GPC of E1 Stage Effluent.

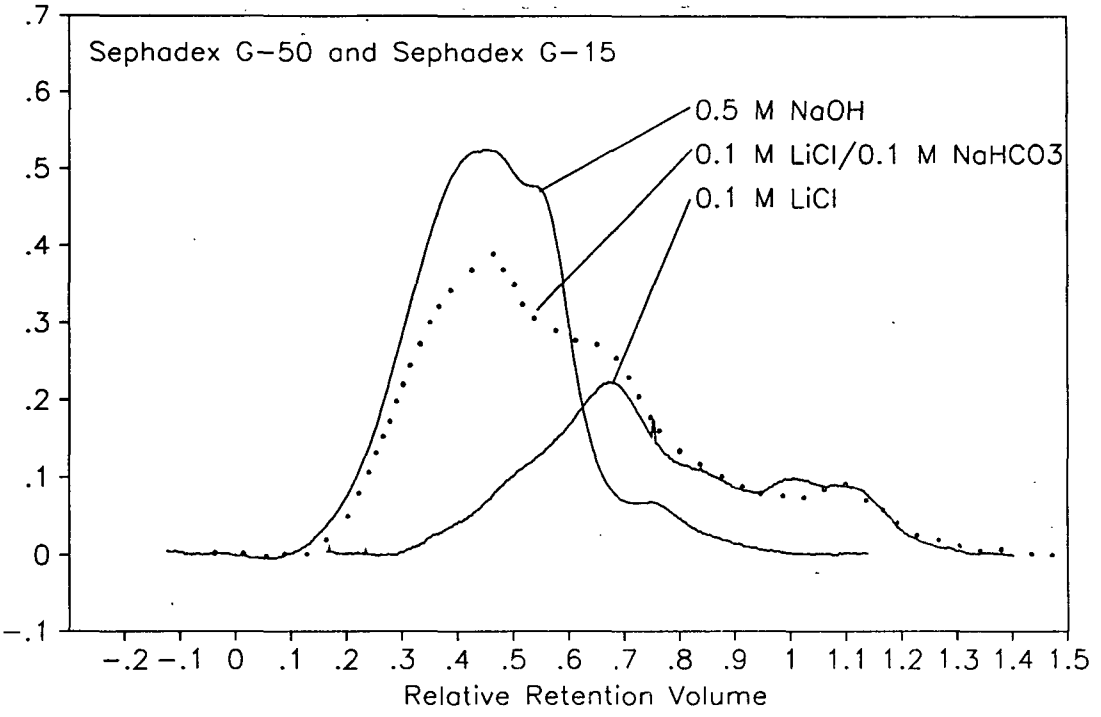

Figure 3. Dual Column GPC of (C+D) Stage Effluent.

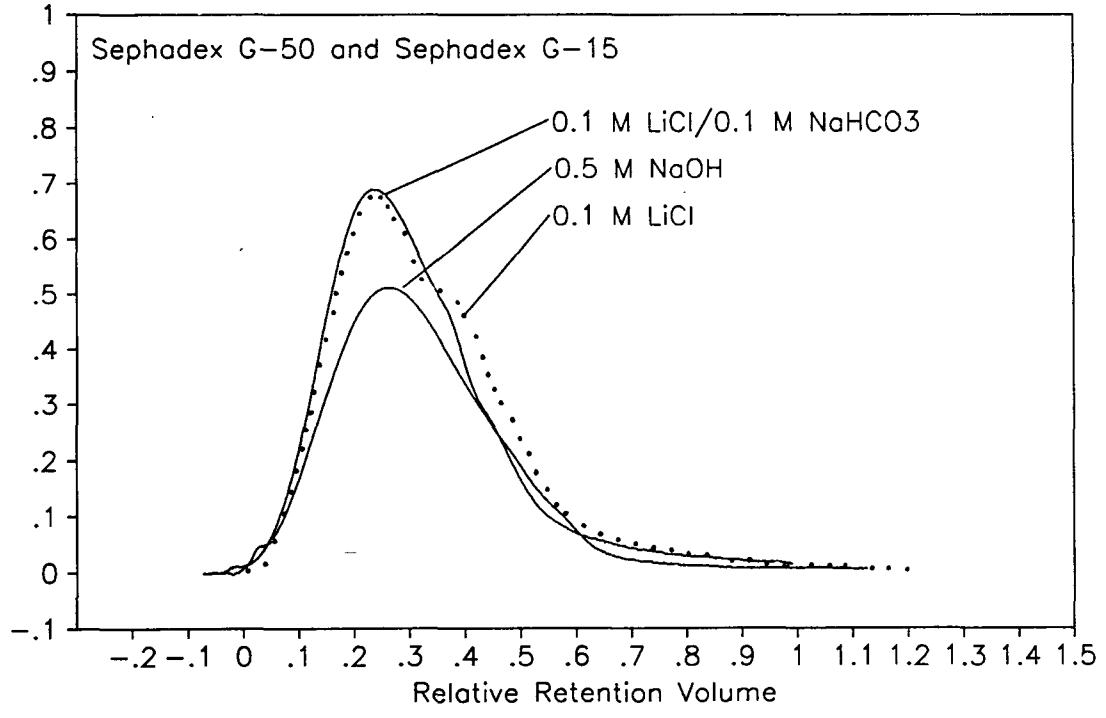

Figure 4. Dual Column GPC of E1 Stage Effluent.

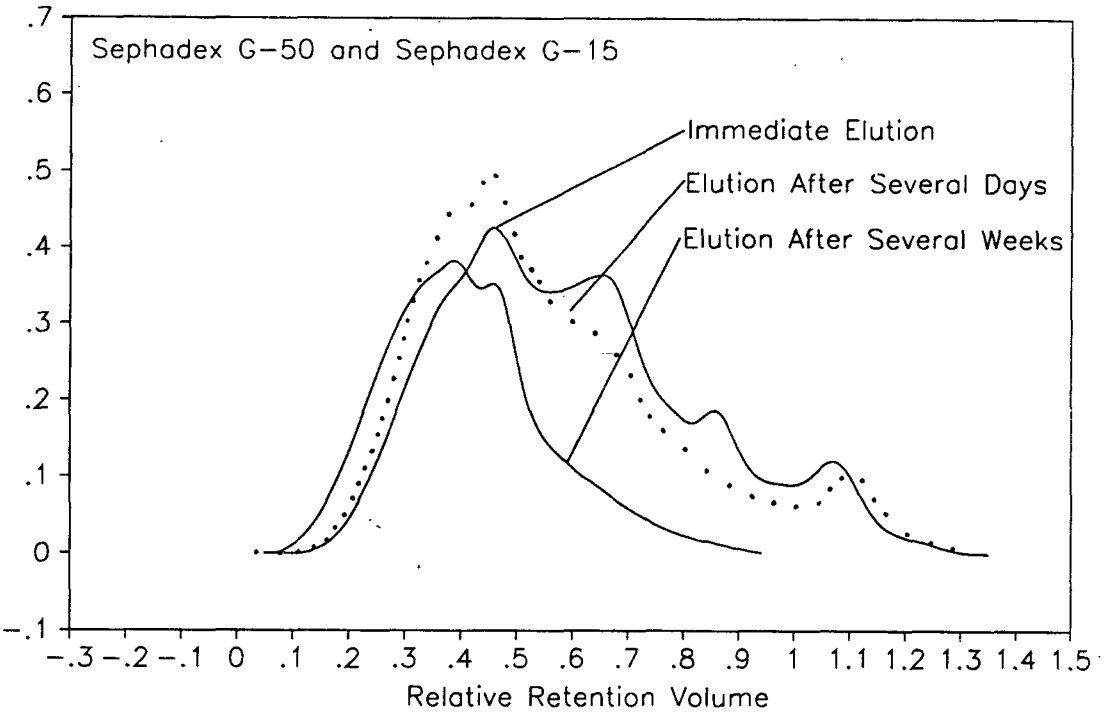

Figure 5. GPC of (C+D) Effluent After Different Storage Times in 0.1 M LiCl/0.1 M NaHCO3.

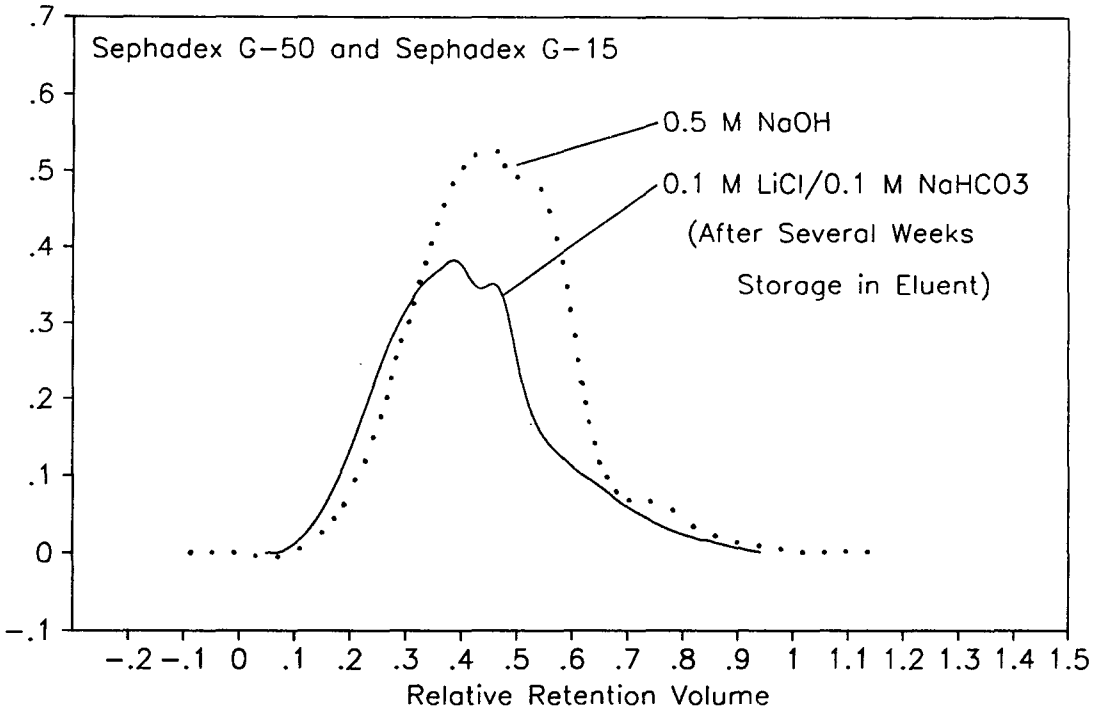

Figure 6. GPC Comparison of (C+D) Effluent–0.5 M NaOH Compared to Lon Storage Time in 0.1 M LiCl/0.1 M NaHCO3.

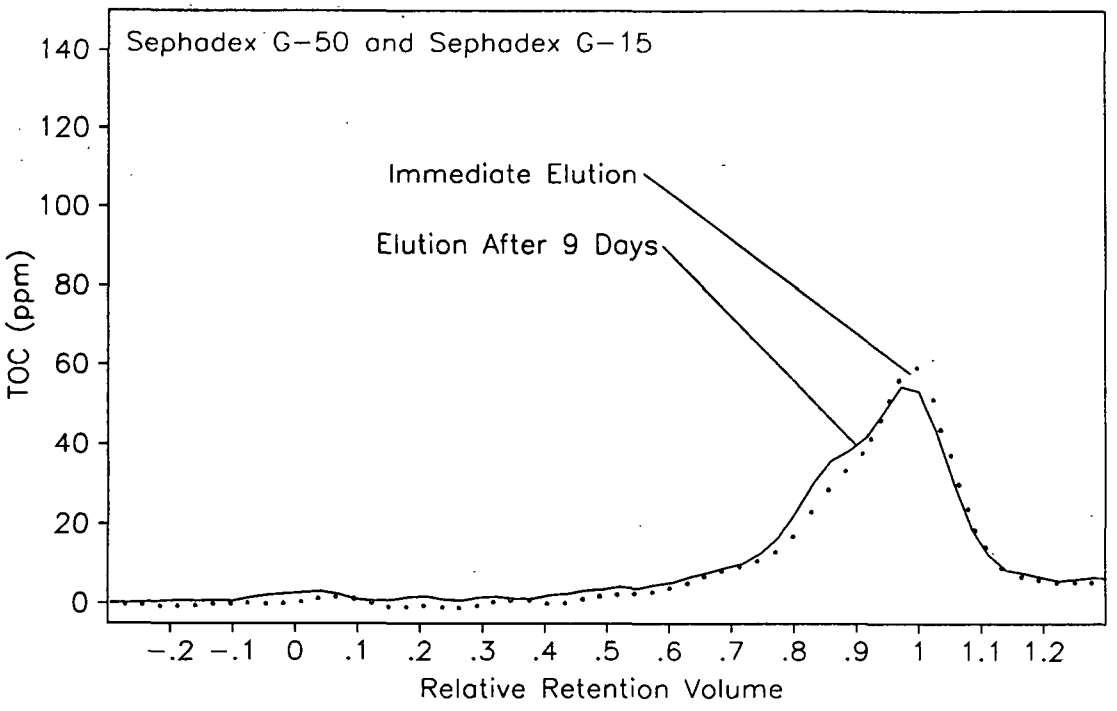

Figure 7. GPC of (C+D) Effluent After Storage in 0.1 M LiCl.

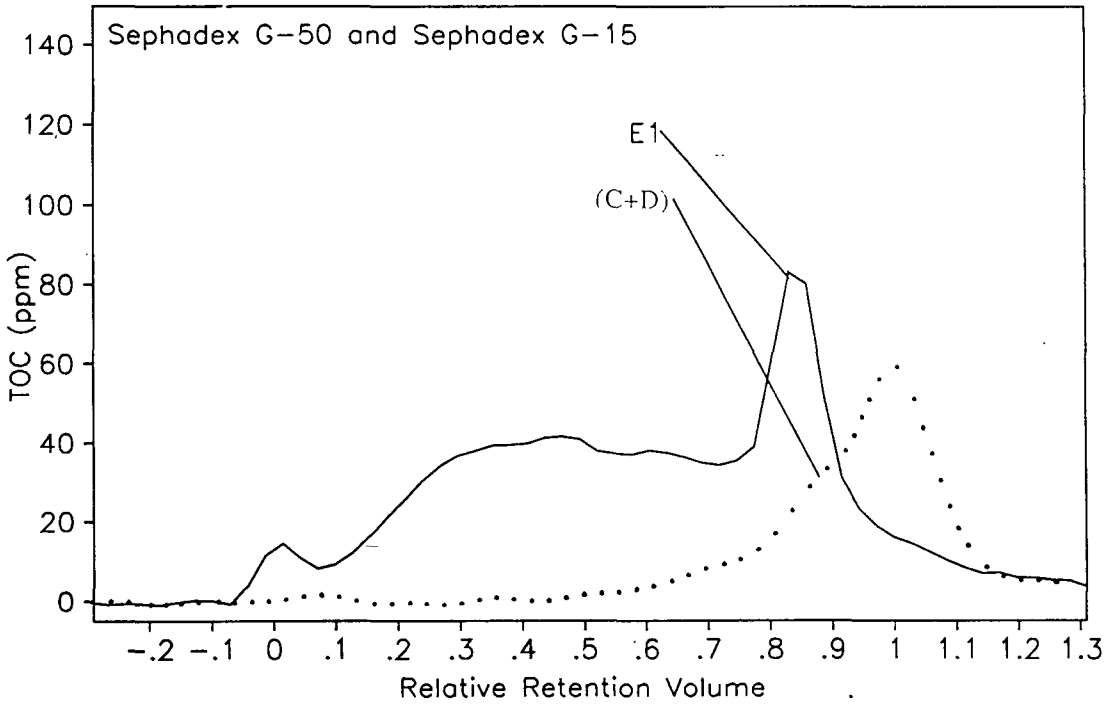

Figure 8. GPC of Effluents with TOC Detection.

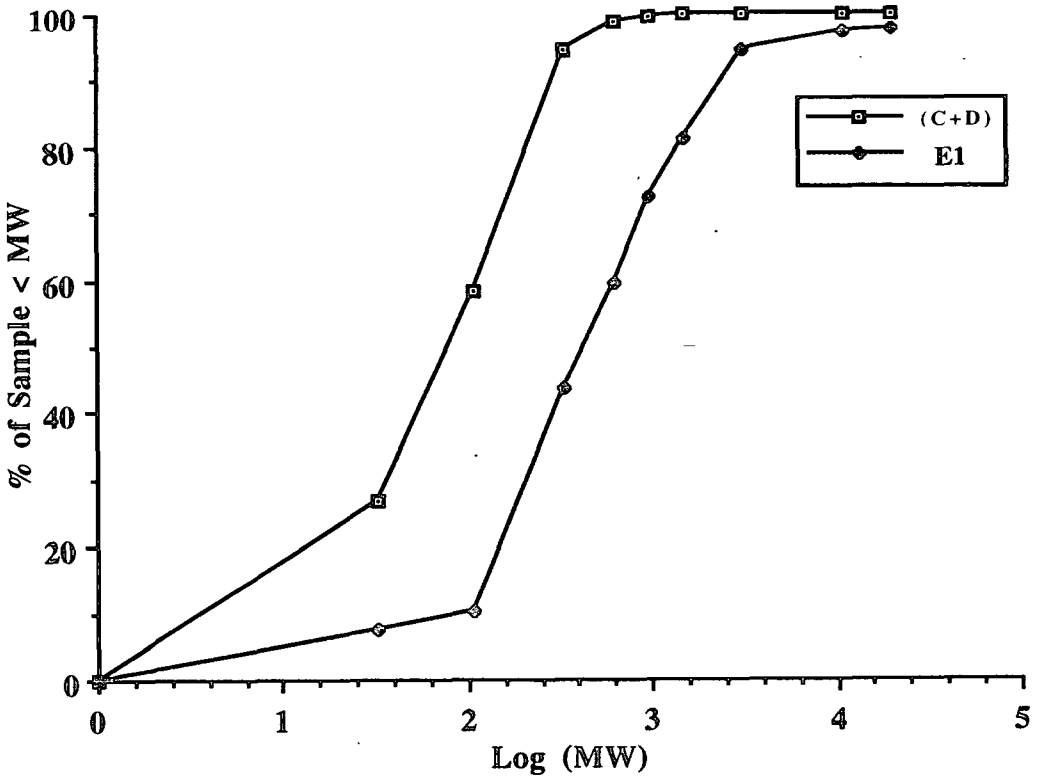

Figure 9. Cumulative Molecular Weight Distributions for Effluents.

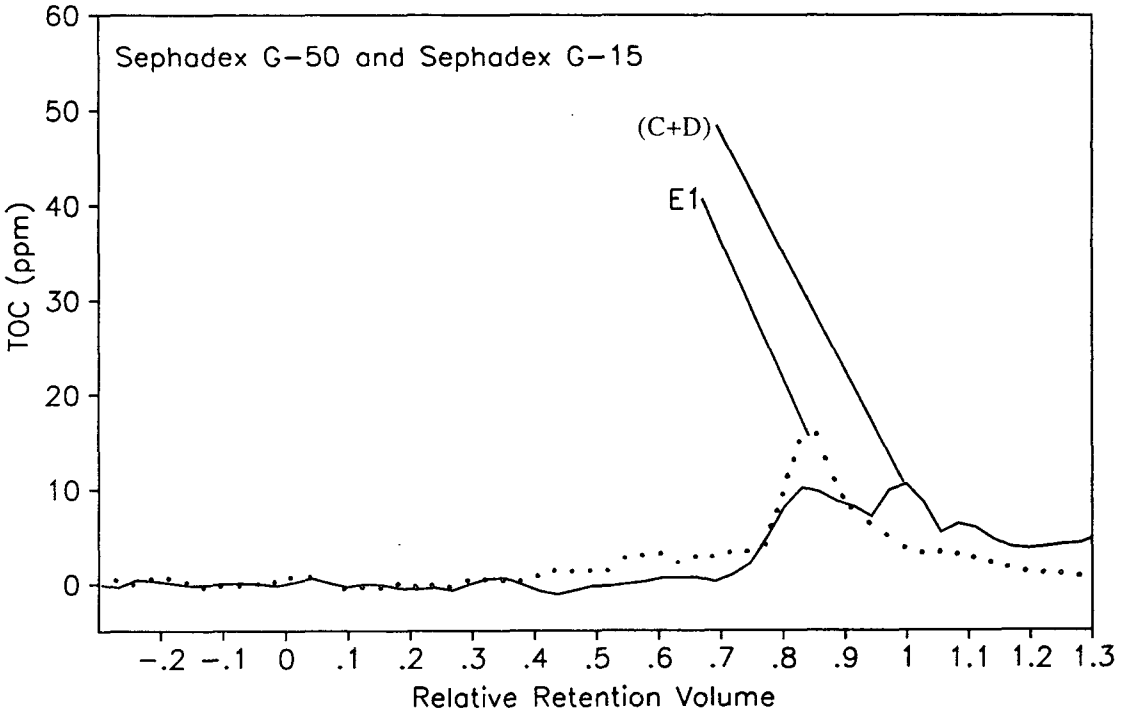

Figure 10. GPC of Ether Extracts.

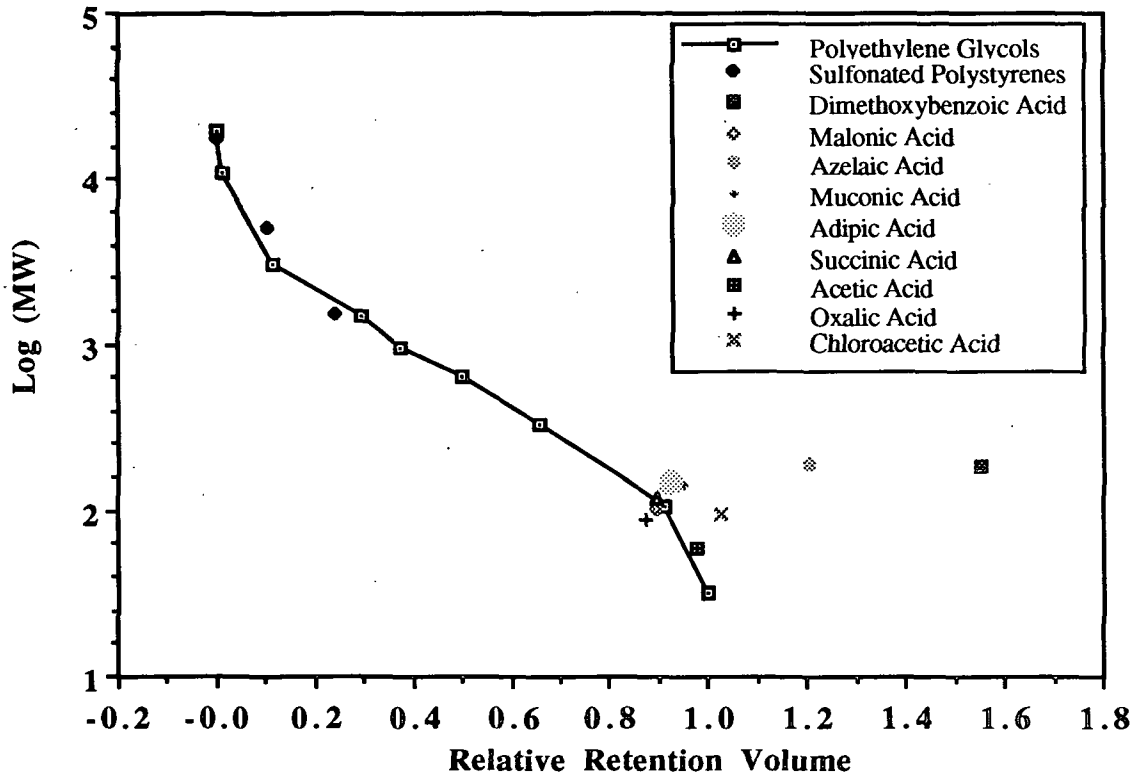

Figure 11. Calibration Curve for Dual Column System.

Table I. Elution of PEG Standards and Methanol.

Molecular Weight	Relative Retention Volume
19,700	0.000
10,900	0.013
3,070	0.115
1,490	0.295
960	0.372
629	0.500
331	0.654
106	0.910
32	1.000

Section 6 Conclusions

This preliminary work led to the development of the GPC method that was used to determine the molecular weight distributions of the effluents.

The GPC method utilized 2 Sephadex gel columns in series, 0.1 N LiCl eluent, and total organic carbon (TOC) detection. The method had several significant advantages over other GPC methods, which allowed it to provide more accurate molecular weight distributions for bleaching effluents. These advantages included increased low molecular weight resolution, elimination of association, and a universal detection system capable of equally determining both lignin and carbohydrate fragments.

Section 7: Molecular Weight Distributions of Effluents from Chlorine Dioxide Delignification

In Section 7 the GPC method that was developed in Section 6, was applied to bleaching effluents. The proportion of low (< 1000) molecular weight material, which is considered environmentally significant, was determined for each effluent.

The use of chlorine dioxide rather than chlorine decreased the proportion of low molecular weight material in both the C or D, and the (EO) stage effluents. The use of oxygen delignification before 100% ClO_2 bleaching increased the proportion of low molecular weight (EO) stage material.

Within the OD(EO) sequence, a D stage begun at pH 4 rather than at pH 2 decreased the proportion of low molecular weight D stage material, but increased the proportion of low molecular weight (EO) stage material. No apparent trend of D stage reaction time on the proportion of low molecular weight (EO) stage material was seen. However, a greater proportion of low molecular weight D stage material was detected at D stage reaction times of 3 seconds and 30 minutes, than at 1 minute and 5 minutes.

MOLECULAR WEIGHT DISTRIBUTIONS OF EFFLUENTS FROM CHLORINE DIOXIDE DELIGNIFICATION

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ABSTRACT

The amount of low molecular weight chlorinated organic material formed during bleaching is a concern because this material has the potential to adversely affect the environment. To study the extent of the formation of low molecular weight material during elemental chlorine free (ECF) bleaching, a method of aqueous gel permeation chromatography (GPC) was developed for the determination of bleaching effluent molecular weight distributions. It employs Sephadex gels, aqueous LiCl eluents, and total organic carbon (TOC) detection.

Softwood kraft pulp was delignified with ClO_2, NaOH, and O_2 and the molecular weight distributions for both the D and (EO) stage effluents were determined. Complete substitution of ClO_2 for Cl_2 decreased the proportion of low (< 960) molecular weight material in the bleaching effluents by 14-18%. Smaller effects resulted from changes in D stage initial pH and reaction time. Oxygen delignification prior to 100% chlorine dioxide bleaching slightly decreased the proportion of low molecular weight material in the (EO) stage effluent.

INTRODUCTION

The molecular weight distribution of bleaching effluents is important from an environmental perspective, because high molecular weight material is not biologically active and may therefore be innocuous. High (> 1000) molecular weight effluent material has been shown to be either non-toxic (1) or less toxic (2) than the low molecular weight fraction, which contains the majority of the effluent's acute toxicity (3). However, low molecular weight material is more readily degraded in biological treatment systems than high molecular weight material (4, 5).

Molecular weight distributions of bleaching effluents have been determined by both ultrafiltration (6-11) and gel permeation chromatography (GPC) (1, 11, 12). The two methods give widely differing results, with GPC detecting more low molecular weight material than ultrafiltration (11). Both methods indicate considerably more high molecular weight material in E stage effluents than in C or D stage effluents (1, 6-9, 12). Several studies have determined the effect of bleaching variables, such as chlorine dioxide substitution (7, 13) or oxygen bleaching (8, 9, 14) on the molecular weight distributions of effluents. It is difficult to draw conclusions from these limited results however, due to the lack of reliability of ultrafiltration which has most often been used in such studies. Ultrafiltration may indicate more high molecular weight material than GPC because of the concentration dependent association that occurs in ultrafiltration (11). Such association can be controlled with GPC. However, GPC has not often been used to investigate the effects of bleaching process variables on the molecular weight distribution of effluents.

A method of aqueous GPC was developed in this laboratory, as described elsewhere (12). The method employs Sephadex gels, aqueous LiCl eluent, and total organic carbon (TOC) detection. This method has several advantages over other GPC methods, including greater resolution, control of association, and a universal detection system. TOC detection is more appropriate than ultraviolet (UV) detection for GPC of bleaching effluents, since effluents may contain carbohydrates and other materials which are not detected by UV.

In the present investigation, this method was used to determine the molecular weight distributions of bleaching effluents produced in the laboratory under well controlled bleaching conditions. The effects of 100% ClO_2 substitution, oxygen bleaching, D stage initial pH, and D stage reaction time were studied.

EXPERIMENTAL APPROACH

Distributions of D and (EO) stage effluents were determined individually. Gel permeation was done using 2 Sephadex columns in series. The first contained G-50 gel and the second contained G-15 gel. The 2-column system was used to achieve improved low molecular weight separation (12). Polyethylene glycol standards of known molecular weight were used to calibrate the system, and all distributions were transformed to a relative retention volume scale based on

high and low molecular weight standards (12). Relative retention volume is calculated as follows:

$$\text{Relative Retention Volume} = R_s - R_h \,/\, R_l - R_h$$

where

R_s = retention volume of sample.
R_l = retention volume of low molecular weight standard.
R_h = retention volume of high molecular weight standard.

TOC Detection

The eluent passes from the columns through a 1 ml flow cell, from which TOC samples are drawn. At each sampling interval, the instrument draws 5 250 µl samples and injects them to the waste stream. This essentially empties the flow cell, and allows it to fill with fresh column eluent containing a new sample. Immediately after the injections to waste, the sample for TOC determination is drawn and analyzed. This process is automatically repeated as often as the TOC instrument can achieve a baseline after TOC measurement (usually every 3-4 minutes). The eluent flow rate was 0.6 ml/minute and total column volume was 200 ml or less during this work. Therefore, a typical experiment lasted 300 minutes or more and consisted of more than 85 individual TOC determinations.

Molecular Weight Distributions

The chromatograms, as originally collected, consisted of pairs of time and TOC data. The data were transformed to the relative retention volume scale, the baseline corrected to zero TOC, the chromatograms integrated to determine eluted TOC, the curves normalized to 1000 µg TOC, and the area between the mean elution values of the standards determined.

This information was used to construct cumulative molecular weight distributions. Such distributions provide an approximate numerical measure of the percentage of effluent TOC below a given molecular weight level. All standards exhibit retention volumes with approximately normal distributions and the center of the distribution was used in determining the cumulative distributions of the effluents. Therefore it is not strictly correct to state that these curves indicate the percentage of material with a molecular weight less than the corresponding molecular weight, since material of a particular molecular weight actually elutes both before and after the mean retention volume of the standard. However, these cumulative distribution curves remain valuable for comparing effluent distributions. They allow quantitative analysis rather than the purely qualitative analysis usually done with this type of data.

Statistical Analysis

Quantitative results allow statistical analysis and determination of significant differences between effluents. A total of 32 samples were analyzed. The D and (EO) stage effluents were produced under 8 different sets of bleaching conditions. Each bleaching sequence was performed twice. In one case, a replicate effluent sample was not available. In this case, the identical sample was run twice. The variation was not distinguishable from that attained with the replicate effluent samples and therefore this replicate chromatogram of the identical sample was used in the analysis. A 2-way analysis of variance was performed on the percentage of material with a molecular weight of less than 960 for each set of bleaching conditions and for both stages. Duncan's multiple range test (15) was used to determine which differences were statistically significant.

RESULTS AND DISCUSSION

The reproducibility of both the bleaching experiments and GPC runs was very good as illustrated in Figure 1. This shows the normalized D and (EO) stage effluent distributions for the OD(EO) bleaching sequence. The D stage distributions represent the 2 replicate chromatograms for the identical effluent, while the (EO) stage distributions represent a single GPC chromatogram for each of 2 replicate effluents.

The relative retention volume scale, which serves as the x-axis for the chromatograms, was determined using high and low molecular weight standards. The relative retention volumes for all molecular weight standards are given in Table I, and the corresponding calibration curve is shown in Figure 2.

The cumulative molecular weight distribution curves given here are based on the mean results of the 2 replicates per set of bleaching conditions. Figure 3 shows replicate cumulative D stage molecular weight distribution data for 5 minute and 3 second D stage reaction times. This figure makes clear how reproducible the cumulative data are, particularly at molecular weight levels of greater than 300. The figure shows that small significant differences can be detected, due to precise data.

The cumulative molecular weight distributions were interpreted principally in terms of the proportion of material with a molecular weight of less than 960, since this is the environmentally significant portion of the effluent. Throughout this paper, the material with a molecular weight of less than 960 will be referred to as "low" molecular weight material.

The Effect of 100% ClO_2 and O_2 Bleaching

Effluents from OC(EO), OD(EO), and D(EO) bleaching of softwood kraft pulps were previously generated (16). The cumulative molecular weight distributions for D or C, and for (EO) stage bleaching effluents from these partial sequences are shown in Figures 4 and 5.

For all 3 sequences, the D or C stage effluents contained a significantly greater proportion of low molecular weight material than the (EO) stage effluents. For example, within the OC(EO) sequence, about 94% of the C stage material was low molecular weight, while only 85% of the (EO) stage material was low molecular weight.

Use of chlorine dioxide to completely replace chlorine decreased the proportion of low molecular weight material in the effluents from both stages. Use of 100% chlorine resulted in about 94% low molecular weight material in the D or C stage compared to about 81% when chlorine dioxide was used. Similarly within the (EO) stage, use of 100% chlorine dioxide decreased the proportion of low molecular weight material from about 85% to 70%. On the basis of these molecular weight distributions, it may be concluded that the environmental benefits of ClO_2 delignification include formation of a decreased proportion of low molecular weight material.

The effect of oxygen bleaching on the effluent molecular weight distribution was not nearly as large but was nevertheless statistically significant. Oxygen delignification preceding 100% chlorine dioxide bleaching increased the proportion of low molecular weight material in the (EO) stage effluent (70 vs. 67%). Although a greater proportion of low molecular weight material was formed in the OD(EO) sequence, on an absolute basis the D(EO) sequence produced more low molecular weight material since about half of the lignin was removed during oxygen bleaching.

The Effect of D Stage pH

Cumulative molecular weight distributions for effluents from the OD(EO) bleaching sequence utilizing 2 initial D stage pH levels (17), are presented in Figures 6 and 7. As previously observed for different bleaching sequences, the D stage effluents contained an increased proportion of low molecular weight material than the (EO) stage effluents.

In the case of the D stage effluents, the D stage begun at pH 2 resulted in 81% low molecular weight material, while the D stage begun at pH 4 resulted in 78% low molecular weight material. However, in the (EO) stage effluents the trend was reversed, with the D stage begun at pH 2 resulting in 70% low molecular weight material and the D stage begun at pH 4 resulting in 74% low molecular weight material. Overall, changing the D stage initial pH over the range of 2 to 4 had little effect on effluent molecular weight distribution.

The Effect of D Stage Reaction Time

Using a specially designed D stage bleaching reactor, effluents were produced by using the OD(EO) bleaching sequence, with D stage reaction times of between 3 seconds and 30 minutes (18). The cumulative molecular weight distributions for the effluents are presented in Figures 8 and 9. Like D stage pH level, D stage reaction time has little effect. Again, the D stage effluents consist of a greater proportion of low molecular weight material than the (EO) stage effluents.

In the case of the D stage effluents (Figure 8), 30 minute and 3 second D stage bleaching times resulted in a significantly greater proportion of low molecular weight material than D stage bleaching times of 5 minutes and 1 minute. The 30 minute and 3 second D stages resulted in about 80% low molecular weight material. The 5 minute and 1 minute D stages resulted in about 75% low molecular weight material. It is reasonable to suppose that in the first 3 seconds of bleaching the most accessible lignin end units are preferentially affected, resulting in an increased proportion of low molecular weight material. Subsequently, higher molecular weight material is removed, while the removed material is simultaneously degraded in solution.

In the case of the (EO) stage effluents (Figure 9), no simple time trend was observed. Although a 30 minute D stage significantly increased the proportion of low molecular weight material compared to 5 min-

utes or 3 seconds, it was not significantly different from the proportion of low molecular weight material produced in the 1 minute D stage. The absence of a time trend suggests that the process of making lignin alkali soluble occurs within the first 3 seconds of the D stage. This is consistent with work (18) that showed that the entire amount of TOC that could be released during caustic extraction, was released after only a 3 second D stage.

Recovery of Effluent TOC

An advantage of GPC with TOC detection is that it allows a determination of effluent recovery from the columns, by comparison of the integrated chromatogram TOC level with the actual measured TOC of the effluent. Any additional TOC due to column degradation or loss of TOC due to adsorption are apparent using TOC detection but would be unnoticed with other types of detection. Table II presents the average recovery for each bleaching sequence and for each stage. TOC losses were generally less than 25%.

EXPERIMENTAL METHODS

Sample Preparation

Effluent samples were stored in the dark, under highly acidic conditions (< pH 2), and at 4°C. Prior to storage, samples were sparged under acidic conditions to remove carbonates. LiCl was added to the samples to adjust its concentration to 0.1 M and the pH was adjusted to 5.0-5.5 prior to chromatography.

Gel Preparation and Column Packing

Sephadex G-type gels, made of crosslinked dextran, were used for GPC work. The gels were purchased in a powdered state and were swelled in 0.1 M LiCl before column packing. Pharmacia HR 16/50 columns were used for GPC work, and a HR 16 column packing reservoir used during the packing process. Each column was packed individually. The swelled gel was added to the column and the packing reservoir and the gel was packed into the column using flow rates and pressures in excess of those used during chromatography experiments. At least 2 column volumes of eluent (200 ml) was passed through the columns under these conditions to stabilize the gel bed. Once the bed was stable, the column top adapter was attached, and the columns used for chromatography.

Gel Permeation Chromatography

Chromatography was done using a Sephadex G-50 column followed by a G-15 column. Eluent flow was maintained through the chromatography system with an Alltech Model 300 LC pump and an attached pulse dampener. Total organic carbon (TOC) detection was done using a Shimadzu Model TOC-5050 total organic carbon analyzer.

SUMMARY AND CONCLUSIONS

Gel permeation chromatography, utilizing aqueous LiCl eluent, Sephadex G-type gels, and TOC detection was used to determine the molecular weight distributions of a series of laboratory produced effluents.

Use of 100% chlorine dioxide rather than 100% chlorine to bleach oxygen delignified pulp, decreased the proportion of low molecular weight material in the bleaching effluents by 14-18%. The decreased proportion of low molecular weight material formed by ClO_2 is significant from an environmental viewpoint, particularly since this material is also much less chlorinated.

Oxygen delignification before 100% ClO_2 bleaching had a significant effect on the proportion of low molecular weight material formed only in the case of the (EO) stage effluent. However, the effect was much smaller, with only about 3% more low molecular weight material formed when oxygen bleaching preceded chlorine dioxide. Although the OD(EO) sequence resulted in a larger proportion of (EO) stage low molecular weight material, on an absolute basis it still produced about half the low molecular weight material as the D(EO) sequence because oxygen bleaching achieved about 50% delignification prior to the D stage.

D stage initial pH had only a small effect on the proportion of low molecular weight material formed. An initial D stage pH of 2 increased the proportion of low molecular weight D stage material, but decreased the proportion of low molecular weight (EO) stage material, compared to a D stage begun at pH 4.

The D stage reaction time also had only a small effect on the proportion of low molecular weight material. Within the D stage, low molecular weight material was removed at short reaction times, followed by the removal of higher molecular weight material. At longer times, the material was possibly degraded, re-

sulting again in a greater proportion of low molecular weight material. On the other hand, the (EO) stage effluent distribution was independent of D stage reaction time.

ACKNOWLEDGMENTS

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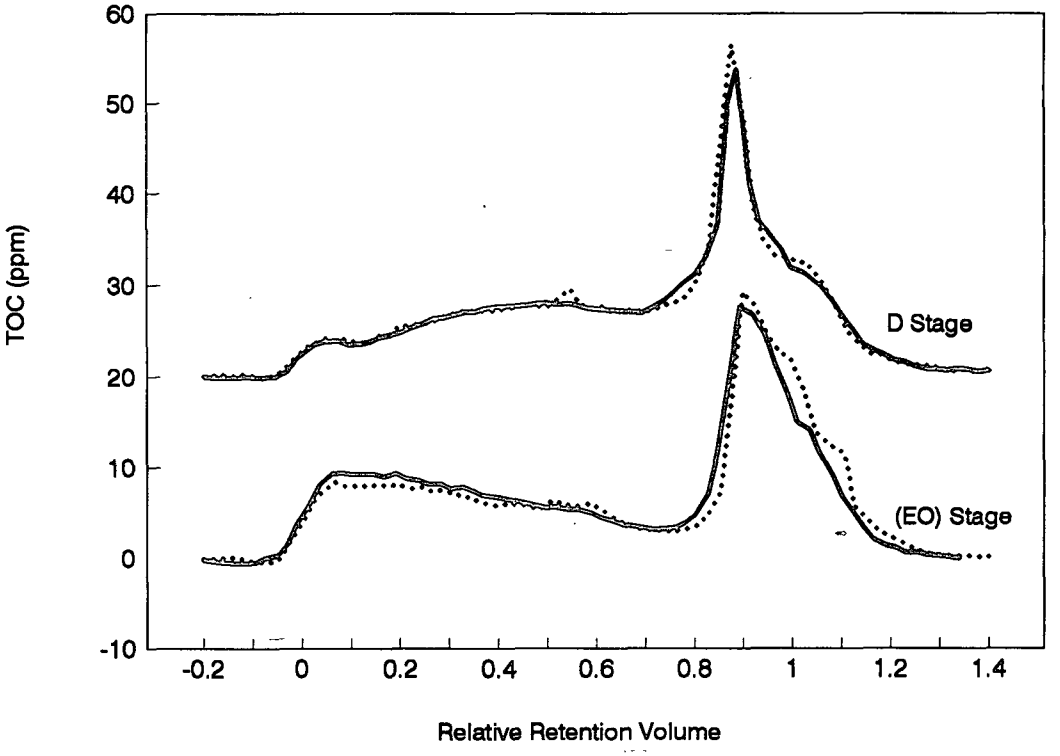

Figure 1. Reproducibility of Chromatograms.

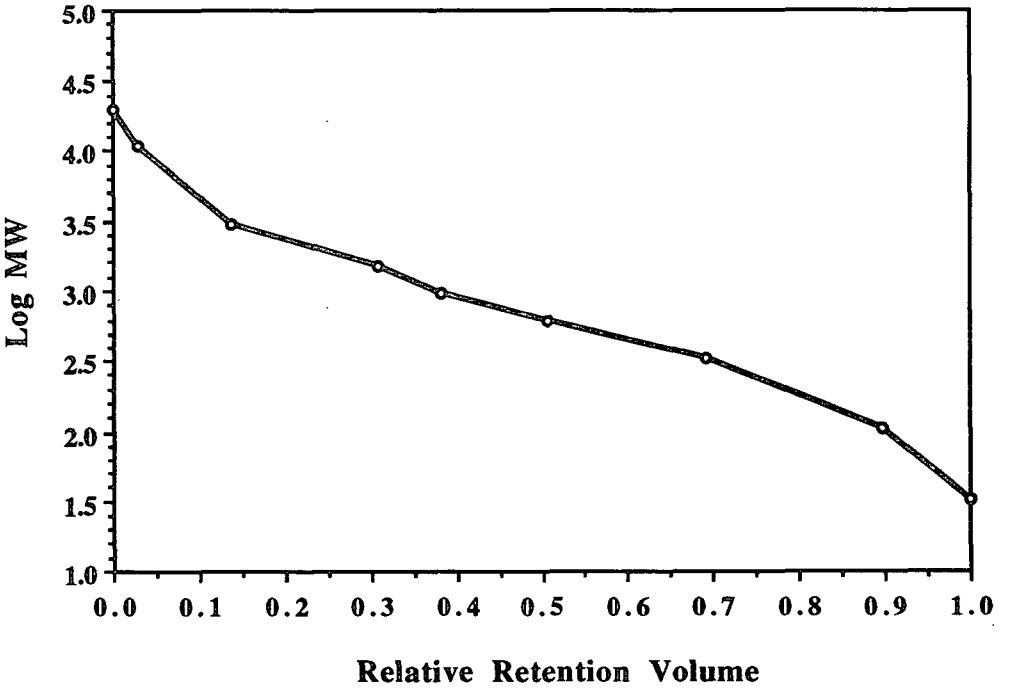

Figure 2. GPC Calibration Curve.

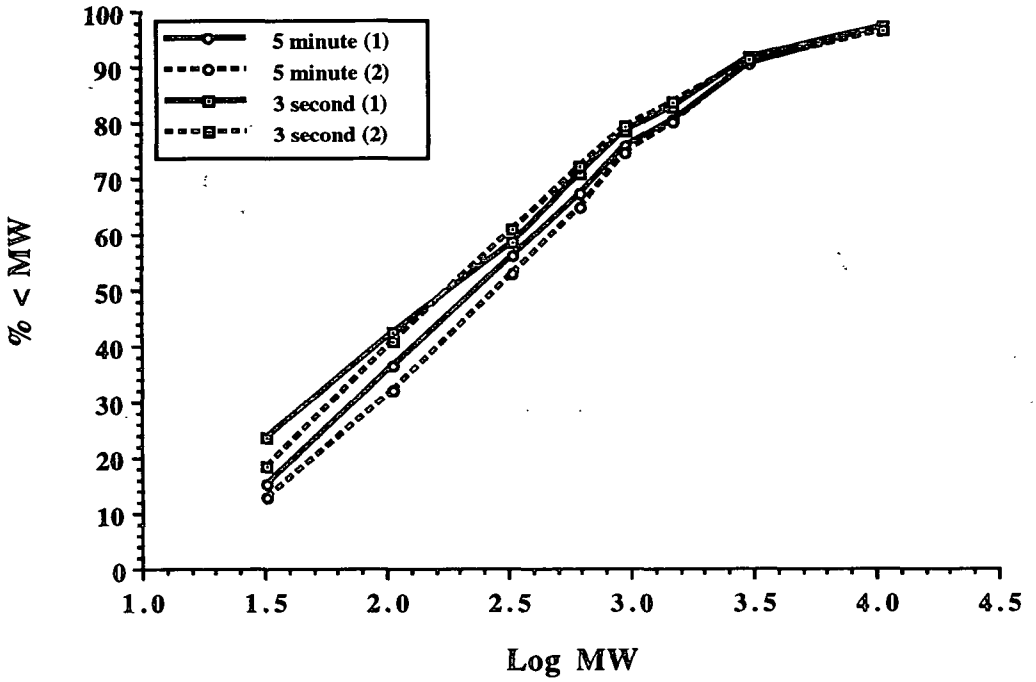

Figure 3. Reproducibility of D Stage Cumulative Molecular Weight Distributions.

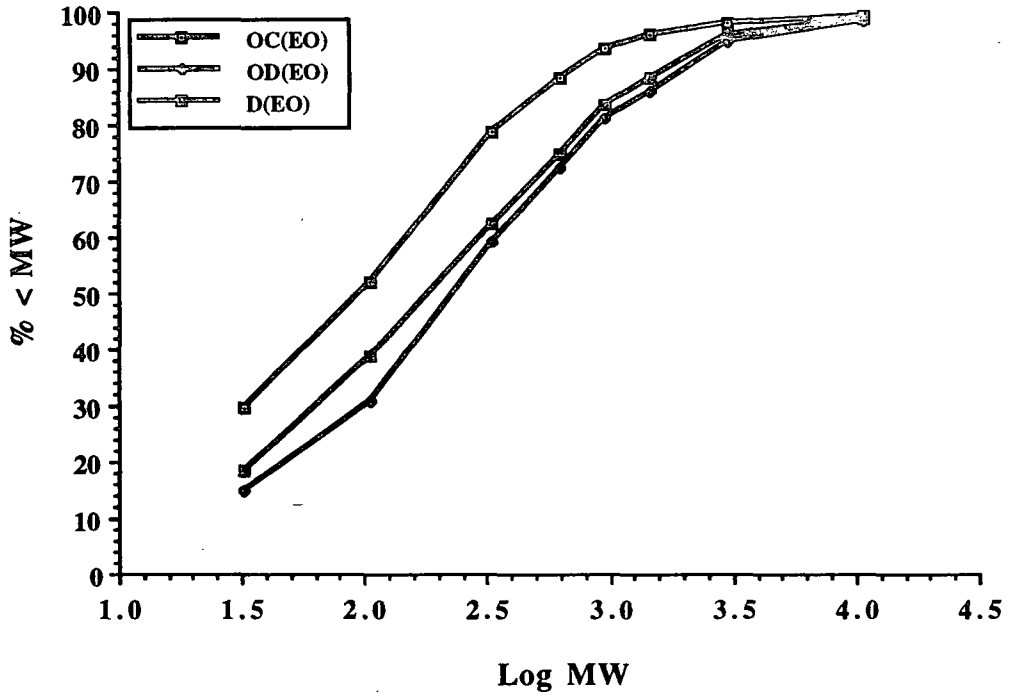

Figure 4. D or C Stage Effluent Cumulative Molecular Weight Distributions.

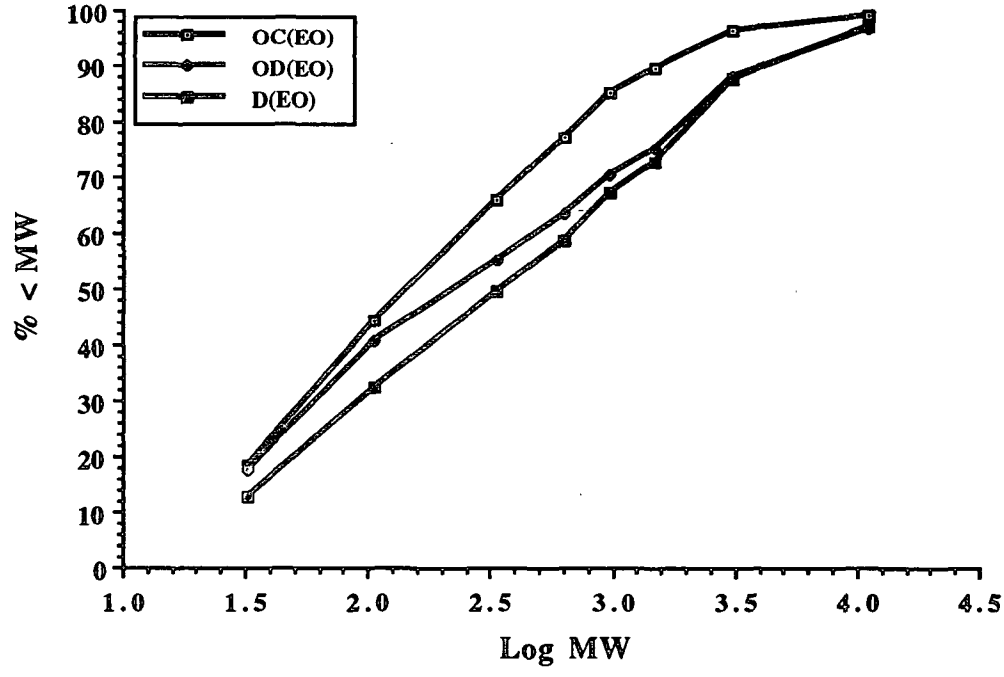

Figure 5. (EO) Stage Effluent Cumulative Molecular Weight Distributions.

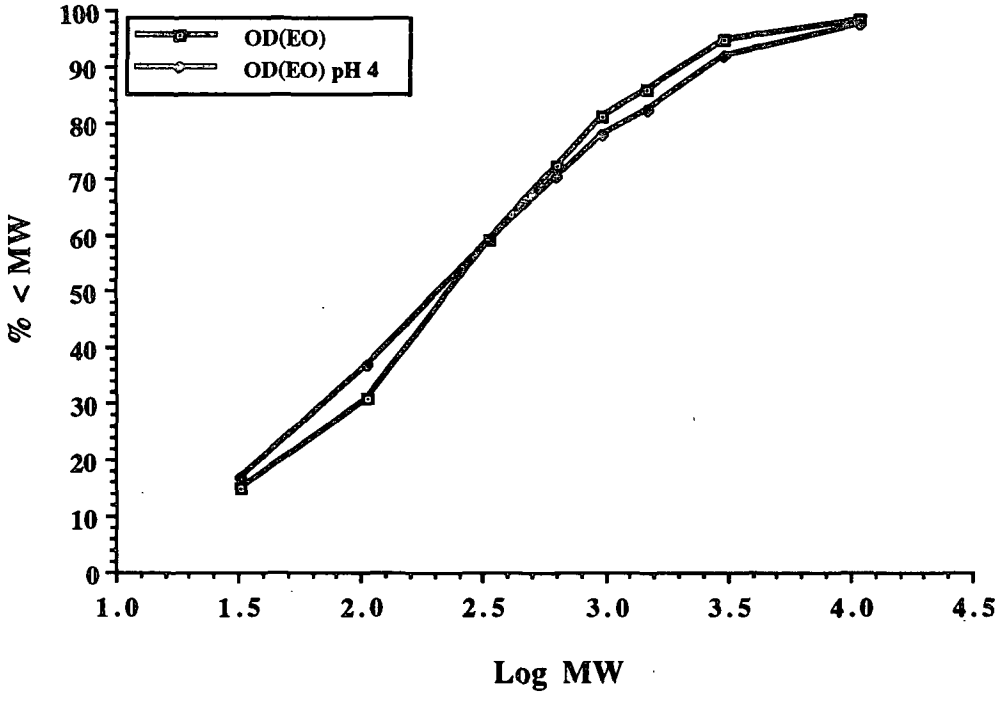

Figure 6. D Stage Effluent Cumulative Molecular Weight Distributions.

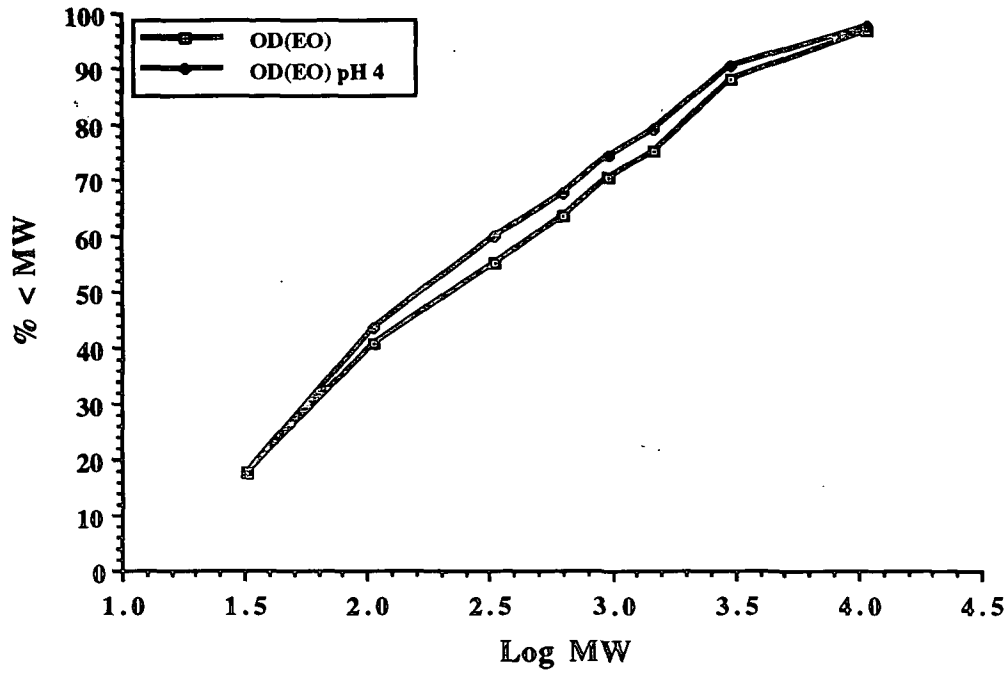

Figure 7. (EO) Stage Effluent Cumulative Molecular Weight Distributions.

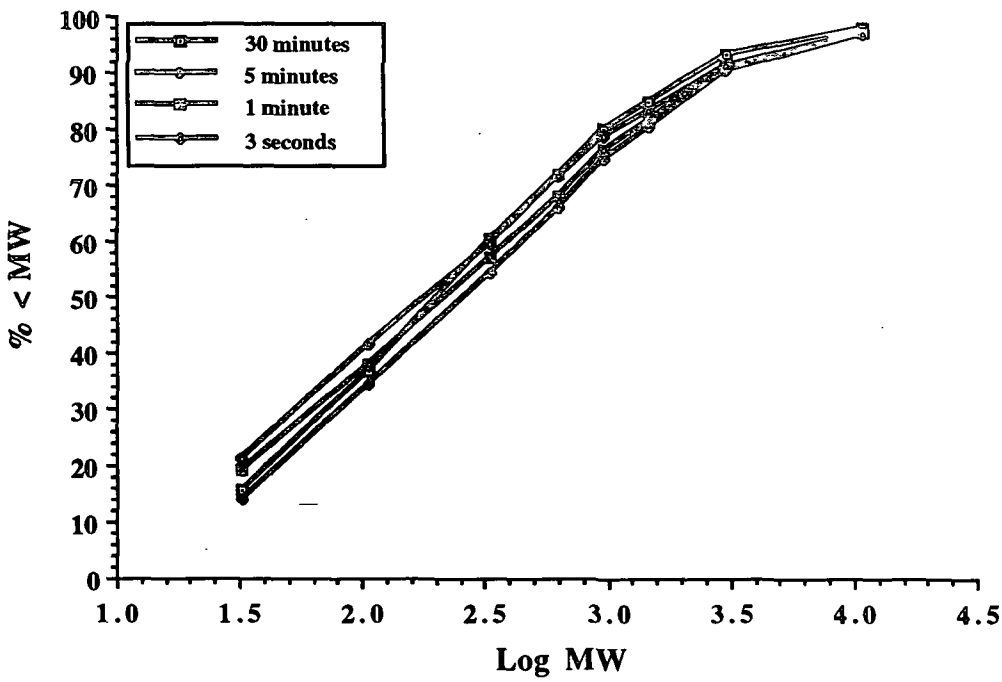

Figure 8. D Stage Effluent Cumulative Molecular Weight Distributions.

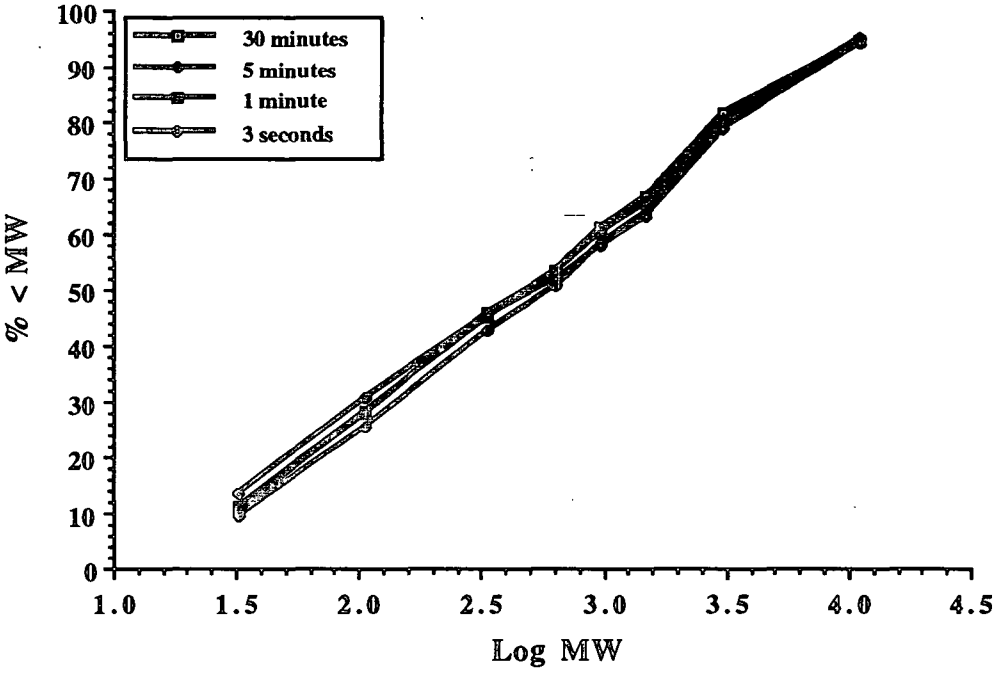

Figure 9. (EO) Stage Effluent Cumulative Molecular Weight Distributions.

Table I. Relative Retention Volume of PEG Standards and Methanol.

Molecular Weight	Relative Retention Volume
19,700	0.000
10,900	0.028
3,070	0.138
1,490	0.308
960	0.383
629	0.506
331	0.691
106	0.897
32	1.000

Table II. Recovery of Effluent TOC.

Bleaching Sequence	D or C Stage Recovery (%)	(EO) Stage Recovery (%)
OC(EO)	75.6	75.7
OD(EO)	85.2	71.7
D(EO)	81.9	76.1
OD(EO)-pH 4 D Stage	78.0	70.3
OD(EO)-30 min D Stage	96.8	77.1
OD(EO)-5 min D Stage	111.8	76.3
OD(EO)-1 min D Stage	98.1	76.6
OD(EO)-3 sec D Stage	104.8	79.0

Section 7 Conclusions

All effluents produced in this research were analyzed by gel permeation chromatography to determine their molecular weight distributions. The proportion of low (< 1000) molecular weight material, which is considered environmentally significant, was determined for each effluent.

The use of chlorine dioxide rather than chlorine decreased the proportion of low molecular weight material in both the C or D, and the (EO) stage effluents. The use of oxygen delignification before 100% ClO_2 bleaching increased the proportion of low molecular weight (EO) stage material.

Within the OD(EO) sequence, a D stage begun at pH 4 rather than at pH 2 decreased the proportion of low molecular weight D stage material, but increased the proportion of low molecular weight (EO) stage material. No apparent trend of D stage reaction time on the proportion of low molecular weight (EO) stage material was seen. However, a greater proportion of low molecular weight D stage material was detected at D stage reaction times of 3 seconds and 30 minutes, than at 1 minute and 5 minutes.

SUMMARY AND CONCLUSIONS

The objective of this thesis research was to determine, in an environmentally relevant and comprehensive manner, the chemical composition of the organic material in pulp bleaching effluents produced by low-AOX bleaching. To achieve this objective, effluent characterization methods were developed and applied to bleaching effluents.

An effluent fractionation scheme was developed and applied to effluents. It consisted of continuous ether extraction of bleaching effluents, fractionation of the ether extract into its acidic, phenolic, and neutral components, and determination of the ratio of chlorine atoms to carbon atoms for all effluents and effluent fractions. The fractionation scheme was based on ether extraction, since the ether extract contains virtually all effluent compounds known to be toxic, mutagenic, and likely to bioaccumulate. The ratio of chlorine to carbon was determined because, within certain classes of compounds, it predicts environmental characteristics such as toxicity and lipophilicity.

Additionally, the molecular weight distributions of bleaching effluents were determined, using a gel permeation chromatography method that was developed during this research. The proportion of low (< 1000) molecular weight material was determined for the effluents. This proportion is significant from an environmental perspective, since low molecular weight material is likely to have greater potential for negative environmental effects than higher molecular weight material.

Effluents produced under bleaching conditions known to reduce the formation of AOX, were characterized using these analysis methods. Three groups of effluents were characterized: Effluents from the OC(EO), OD(EO), and D(EO) bleaching sequences, effluents from the OD(EO) bleaching sequence with the D stage begun at two pH levels, and effluents from the OD(EO) bleaching sequence with D stage reaction times of different duration.

100% ClO_2 SUBSTITUTION AND O_2 DELIGNIFICATION

Characterization of effluents from the OC(EO), OD(EO), and D(EO) bleaching sequences allowed a determination of the effect of 100% ClO_2 substitution and O_2 delignification on the chemical composition of the organic material in bleaching effluents.

100% ClO_2 Substitution

Complete replacement of chlorine with chlorine dioxide may be more environmentally beneficial than indicated by the AOX reduction (Sections 3 and 7). The use of chlorine dioxide instead of chlorine reduced the proportion of material in the environmentally significant ether soluble and phenolic fractions, for both the C or D, and the (EO) stage effluents. In addition to a decreased proportion of material in these fractions, use of ClO_2 also sharply reduced the ratio of chlorine to carbon of the organic material in these fractions. Since both a decreased quantity of material within these fractions and a decreased chlorine to carbon ratio may be expected to relate to a reduced environmental threat, chlorine dioxide use provided two environmental benefits compared to chlorine use. Use of 100% chlorine dioxide instead of chlorine also sharply reduced the ratio of chlorine to carbon in the environmentally significant neutral fraction, for both the C or D, and the (EO) stage effluents.

Replacement of chlorine with 100% chlorine dioxide decreased the proportion of low molecular weight material in both the C or D, and the (EO) stage effluents. Since a decreased amount of low molecular weight effluent material may also be expected to relate to a reduced environmental threat, the use of chlorine dioxide provided yet another environmental benefit.

O_2 Delignification

The use of oxygen delignification prior to 100% chlorine dioxide bleaching may similarly provide more environmental benefits than the AOX reduction suggests (Sections 3 and 7). The use of O_2 delignification reduced the total effluent load, including total AOX, by about half. In addition to a reduction in the total effluent load, the use of oxygen delignification before 100% chlorine dioxide bleaching reduced the ratio of chlorine to carbon in the environmentally significant phenolic and neutral fractions, for both the D and the (EO) stage effluents.

The proportion of low molecular weight (EO) stage effluent increased slightly (about 3%) when oxygen delignification preceded 100% ClO_2 bleaching. Since oxygen delignification reduced the effluent load by about 50%, this slight increase in the proportion of low molecular weight material was of little consequence. On an absolute level, the OD(EO) sequence still produced about 50% less low molecular weight (EO) stage material.

D STAGE pH IN OD(EO) BLEACHING

For the OD(EO) bleaching sequence, beginning the D stage at pH 4 rather than 2, may have both environmental and economic benefits (Section 4). These benefits are based entirely on the increased delignification per unit of applied oxidant that occurred when the D stage was begun at pH 4. The increased level of delignification at a given ClO_2 charge, that occurred when the D stage was begun at pH 4, could allow a reduction in ClO_2 charge while maintaining delignification. The decreased charge can provide ClO_2 savings and an associated cost benefit. A decreased charge of chlorine-containing chemical per unit of lignin will decrease the ratio of chlorine to carbon for all effluent

material, and may therefore provide an environmental benefit, or at the very least a decrease in the level of AOX.

No beneficial effect on effluent composition was apparent at either initial pH level. The environmentally significant ether soluble and phenolic fractions contained an increased proportion of material when the D stage was begun at pH 4, but the ratio of chlorine to carbon within the fractions was decreased under these conditions. The levels of ether soluble and phenolic AOX therefore remained unchanged.

The molecular weight distribution data suggested no environmental advantage for either initial pH level. The differences in the proportion of low molecular weight material for the two initial pH levels were quite small (3-4%). When the D stage was begun at pH 4 rather than 2, a decreased proportion of low molecular weight material was found in the D stage effluent, but an increased proportion of low molecular weight material was found in the (EO) stage effluent.

D STAGE REACTION TIME IN OD(EO) BLEACHING

For the OD(EO) bleaching sequence, a short duration D stage (1 minute or less) may cause environmental benefits in addition to a reduction in the level of total AOX (Section 5). At short reaction times the proportion of material in the environmentally significant ether soluble fraction was decreased, and at the same time the ratio of chlorine to carbon was sharply decreased for this fraction. In addition, at 1 minute of D stage reaction time the proportion of ether soluble AOX (assumed to be "bad" AOX) reached a sharp minimum. All 3 represent environmental advantages for short duration D stages. These effects were due primarily to the acidic subfraction of the ether soluble material, since the same trends were repeated for the acidic fraction.

No apparent environmental advantages existed for any D stage reaction time based on the molecular weight distributions. For both D and (EO) stage effluents, the proportion of low molecular weight material varied by a maximum of about 5% from reaction time to reaction time. For the D stage effluents, a greater proportion of low molecular weight material occurred at both 3 seconds and 30 minutes of D stage reaction time than at 1 and 5 minutes. This suggests initial removal of small fragments, followed by removal of large fragments, followed still later by degradation of the large fragments to small fragments. No time related trend was observed for the (EO) stage effluents.

INDUSTRIAL IMPLICATIONS

The use of a combination of a short duration D stage and an initial D stage pH of 4 within the OD(EO) bleaching sequence, could allow environmental improvement and compliance with proposed U.S. EPA effluent guidelines.[4] It could also provide capital and operating cost savings.

The use of both 100% ClO_2 to replace chlorine, and the use of oxygen delignification before 100% ClO_2 bleaching both may provide greater environmental benefits than indicated by the AOX reduction. This is due to the simultaneous reduction in both the proportion of material within environmentally significant effluent fractions and the chlorine to carbon ratio of the material in these fractions. Additional environmental benefits may be achieved by decreasing D stage reaction time, or by beginning the D stage at pH 4. This research provides additional evidence that ECF technologies are highly effective at reducing the potential environmental threat caused by pulp bleaching.

Under the appropriate conditions, the level of AOX in ECF bleaching effluents can be sharply reduced while extensive delignification is maintained. As indicated in Section 5, the OD(EO) sequence, a D stage of one minute or less duration achieved up to

85% of the total 30 minute delignification while it produced only 40% of the AOX. Under these conditions, the total AOX produced by the OD(EO) partial bleaching sequence was less than 0.2 kg/ton of pulp, which is near the level of the proposed limits.[4] A further decrease in the level of AOX may be achieved by utilizing an initial D stage pH of 4 along with short duration D stages.

Chlorine dioxide bleaching, utilizing both a short duration D stage and an initial D stage pH level of 4, may also provide economic benefits. The initial D stage pH of 4 may allow more delignification per unit of chlorine dioxide, and chemical savings. A short duration D stage may allow capital cost savings, since one minute or less D stage reaction time requires no bleach tower, only a mixer and pipes to retain the slurry during its short retention time.

RECOMMENDATIONS FOR FUTURE WORK

Future work should focus on the mill application of short retention time D stage bleaching, since this technology could provide environmental benefits, cost savings, and compliance with AOX limits. All experiments should utilize full bleaching sequences which are done to either final kappa or final brightness endpoints, and combined effluents from all stages should be analyzed. This would make the future work more applicable to the industry.

Short retention time D stage bleaching should be tested as a part of full bleaching sequences, to determine if pulp of acceptable brightness and strength can be achieved. Final bleaching with both chlorine dioxide and non-chlorine chemicals such as hydrogen peroxide, or combinations of the two, should be done. Strengthening of the (EO) stage after the short duration D stage could help achieve the needed level of delignification. The (EO) stage can be strengthened by increasing the temperature to 90°C or more, and by addition of hydrogen peroxide. Important questions that must be answered include: Can a high quality pulp be produced using short retention time D stage bleaching, while maintaining the environmental benefits observed in the OD(EO) partial sequence? Does the level of AOX in the combined effluent remain near that of the proposed limits, or do final bleaching stages contribute high levels of AOX to the effluent? Is a high level of chlorine bound to the pulp during short retention time D stage bleaching?

A group of experiments should determine if reduced chemical charges can be applied with short duration D stages, while maintaining extensive delignification. It is extremely wasteful to have a high oxidant residual at the end of the D stage. The minimum level of applied oxidant that achieves the necessary level of delignification in a short duration D stage must be determined. Mill application is unlikely if the residual oxidant level is not low.

The effect of D stage initial pH during short retention time D stage bleaching should be determined as well. Since the initial D stage pH of 4 delignified more extensively during a 30 minute reaction period, perhaps it would also delignify more extensively during short duration D stages.

METHODS

The experimental work consisted of 3 general types: Pulp bleaching, the ether extraction-based effluent fractionation, and gel permeation chromatography. Each topic is considered in the following section.

PULP BLEACHING

A 26.0 kappa unbleached southern softwood and a 14.1 kappa O_2 delignified southern softwood were used in this research. Both pulps were produced at the same mill. The unbleached pulp was collected just before the O_2 stage, and the O_2 delignified pulp was collected just after the O_2 stage. Each pulp was well washed before bleaching. The kappa number of both pulp samples was determined using Tappi Standard Method T-236 cm-85.[170]

Preparation of Bleaching Oxidants

Chlorine water was prepared by saturating de-ionized water with chlorine gas. Chlorine was collected in an amber bottle containing 4 L of chilled de-ionized water.

Aqueous chlorine dioxide solution was prepared by the chemical reduction of sodium chlorate with oxalic acid under highly acidic conditions, similarly to the industrial generation of chlorine dioxide.[18] Sixty-seven grams of $NaClO_3$ and 63 g of oxalic acid were added to a 3 L round bottom flask, and heated to 60°C with a water bath. Reaction was started by addition of 167 ml of H_2SO_4 solution (prepared as 120 ml concentrated H_2SO_4 added to 400 ml water and cooled to room temperature). The white crystalline

starting materials emitted green/yellow gaseous chlorine dioxide. The reaction took about 1 hour.

Gaseous chlorine dioxide was swept from the reaction vessel by nitrogen gas and by the CO_2 formed by the decomposition of oxalic acid. Chlorine was removed using a gas washing bottle containing room temperature water. Chlorine dioxide was collected in an amber bottle containing 4 L of chilled de-ionized water. The solution was kept cold with ice water. Only glass and teflon contacted ClO_2 during generation. Teflon tape was used around ground glass joints to prevent leaks. All generation was done in a fume hood, and a shield was kept in front of the generating equipment when in use.

Titration of Bleaching Oxidants

Iodometric titration was used to determine the concentration of both Cl_2 and ClO_2 in oxidant solutions.[18] Iodometric titration consists of addition of KI to an oxidant solution, titration of the solution with $Na_2S_2O_3$ until the yellow color disappears, acidification of the solution, and titration to the starch-iodine endpoint.

Preparation of 100% Chlorine Dioxide

Any chlorine present in the chlorine dioxide solution was converted to ClO_2 by reaction with sodium chlorite. Two moles of $NaClO_2$ were added per mole of Cl_2 in the solution.

C or D Stages of Bleaching

All C or D bleaching stages were done in a 20 L batch reactor that was specially designed to rapidly add bleaching chemicals. In all experiments a cold solution of ClO_2 was injected into a hot pulp slurry. This was done to prevent any volatilization of ClO_2 before injection. Details regarding C and D stage pulp bleaching are given in the Experimental Methods in Sections 3-5 and in Appendices 1 and 2. Bleaching procedures were slightly different in each section.

Actual bleaching conditions for all D or C stage bleaching experiments are given in Appendix 3. Total Active Chlorine (TAC) is given by the sum of the weight of chlorine and 2.63 times the weight of chlorine dioxide, and is expressed as both grams of TAC and as a weight percentage applied to the pulp. An equation for estimating the initial slurry temperature required to achieve the desired final slurry temperature appears in the Appendix, and is given here:

$$T_f = T_i(1+(W_c/W_h))$$

where

T_f = final slurry temperature (^oC)
T_i = initial slurry temperature (^oC)
W_c = weight of cold ClO_2 solution (g)
W_h = weight of hot slurry (g)

The equation was used to calculate the final slurry temperature in the Appendix. The final slurry temperature was also measured.

(EO) Stages of Bleaching

All (EO) stages were done in a Quantum Technologies high shear mixer. Details on (EO) stage pulp bleaching are given in the Experimental Methods of Sections 3-5 and in Appendices 1 and 2.

(EO) stage bleaching conditions are given in Appendix 3. The applied caustic charge (expressed as weight percentage on pulp) was 0.55 times the applied TAC charge (expressed as weight percentage on pulp). The actual caustic charge was calculated by the following formula from Appendix 3:

$$\text{NaOH Charge (\% on pulp)} = VC(100/P)$$

where

V = caustic charge (L)
C = caustic concentration (g/L)
P = pulp weight (g)

The applied O_2 charge (expressed as weight percentage on pulp) was calculated by the following formula from Appendix 3, which is based on the ideal gas law:

$$O_2 \text{ Charge (\% on pulp)} = PV(0.4365)$$

where

P = O_2 pressure (atmospheres)
V = O_2 volume (L)

ETHER EXTRACTION BASED FRACTIONATION

Most experimental details of the ether extraction based effluent fractionation scheme are given in Sections 3-5 and in Appendices 1 and 2. This includes details about effluent preparation, ether extraction, extract fractionation, ether removal, and TOC and AOX analysis of the samples. Additional details are given here.

All effluents and effluent fractions were acidified to a pH of 2 or less using concentrated sulfuric acid, and were stored at 4°C, in the dark, and in sealed amber bottles. AOX and TOC analyses were done on each whole effluent and on all effluent fractions. Molar ratios of chlorine to carbon were determined from these measurements.

TOC Analysis

The TOC analyzer was calibrated using solutions of potassium hydrogen phthalate. Seven samples were used to prepare a calibration curve over the range of 0 to about 250 ppm TOC. A second degree polynomial was fit to the curve of TOC versus detector response. The slightly non-linear calibration was very reproducible over the course of this research, and was probably due to imperfections in the highly worn infrared detection system of the TOC instrument.

Four injections of each sample were made, and the mean recorded if the standard deviation of the output was less than 1 voltage unit. If the standard deviation was greater, the injection procedure was repeated until the standard deviation was below 1. Mean output voltages were recorded for each effluent, and TOC concentrations were determined using the calibration curve. To prevent any systematic variation due to instrument drift, all samples and standards were run in random order.

For quality control purposes, the mean recovery of the middle calibration standard (usually a 125 ppm TOC standard) was charted. Mean and moving range control charts and all control chart data are presented in Appendix 4. Appendix 4A shows that the TOC recovery remained within statistical control over the course of these experiments, and the average recovery was 100.6%. Appendix 4B shows that the moving range for the data was also within statistical control. Moving range was used to determine sample to sample variation, since only a single value for standard recovery was obtained at each sampling interval. Control chart data are presented in Appendix 4C.

AOX Analysis

Both 2,4,6-trichlorophenol standards and method blanks were tested for quality control purposes. All sample, standard, and blank AOX determinations were reported as mean values of 3 replicates. The level of AOX within samples is given by the mean sample determination minus the mean method blank value. Effluent samples were run in complete blocks containing one replicate of each sample. Each block included one standard and one blank. Samples were run in random order within the blocks.

The AOX method blank values are charted in Appendix 5. Appendix 5A shows the mean control chart for AOX blanks. The narrow control limits indicate the very good precision of the blanks. However, the mean blank varied widely over time and was out of statistical control most of the time. The range chart (Appendix 5B) was generally in control, again indicating good precision. Blank control chart data are presented in Appendix 5C.

Reasons for the wide blank variation may include the background AOX levels of the activated carbon, the polycarbonate filters and especially the water supply. Although the blanks varied widely over a long period of time, this variation did not affect AOX results since the blank value was subtracted from all samples. If the blank was high for example, all samples analyzed at that time were also high by a corresponding amount.

AOX standard recovery is charted in Appendix 6. Appendix 6A shows a mean AOX standard recovery of 98.3% over the course of these experiments. Although standard recovery was out of statistical control at times, it still fell well within the level of variation allowed by the standard methods.[16, 17] Appendix 6B shows the range chart, which was generally in statistical control, indicating good precision in analyses. Appendix 6C presents the AOX standard control chart data.

AOX and TOC Balances

AOX and TOC data were entered into a Lotus 123 spreadsheet for calculation of molar carbon to chlorine ratios, and the AOX and TOC content of each fraction expressed in kg/tonne of pulp. The spreadsheet formulas and instructions for their use are given in Appendix 7. The output from the spreadsheet is presented in Appendix 8A for all bleaching effluents, and in Appendix 8B for model compound studies. Carbon and chlorine mass balances are given in these printouts, for both the balance around the ether extraction and around the extract fractionation. The balance around the fractionation scheme is given by the sum of TOC or AOX in the NVEE I, NVEE II, and NVNEE fractions divided by the NVW effluent TOC or AOX, and expressed as a percentage. The balance around the ether extract fractionation is given by the sum of AOX or TOC in the NVEEA, NVEEP, and NVEEN fractions divided by the NVEE I fraction AOX or TOC, and expressed as a percentage. The balances generally showed between 90 and 110% recovery of TOC and AOX, with the exception of several carbon balances showing 120% or greater recovery, and several chlorine balances showing less than 80% recovery. High carbon balances were probably due to incomplete ether removal, while low chlorine balances were probably due to alkaline dechlorination during sample preparation.

Statistical Analysis of Results

Analysis of variance (using NCSS statistical software) was performed on all fractionation results and was done as explained in Sections 3-5 and in Appendices 1 and 2. Analyses of variance were also done on the preliminary AOX method development data in Section 1, and on the determination of extractor to extractor variation in Section 2.

Appendix 9A presents the analyses of variance for Section 1 preliminary AOX method development work, Appendix 9B presents analysis of variance results for the ex-

tractor to extractor variation comparison, Appendices 9C, 9D, and 9E present analyses of variance results for all effluent fractionation results presented in Sections 3-5 and in Appendices 1 and 2. Appendix 9F presents the analysis of variance results for the ratio of TOC to the change in kappa number, presented in Sections 3-5 and in Appendices 1 and 2.

Appendix 10 presents tables of significant differences observed in the results from Sections 3-5 and Appendices 1 and 2, based on analyses of variance in Appendices 9C, 9D, and 9E. Appendices 10A-10C correspond to Sections 3-5. In each table the comparison of interest is indicated by a letter which corresponds to that comparison. For example, in Appendix 10A the letter A refers to the comparison of the OC(EO) and OD(EO) sequences. The presence of a significant difference is indicated by the confidence level (for example, 90% or 95%) If the comparison of interest was not significant, it is indicated by an N.

GEL PERMEATION CHROMATOGRAPHY

Most experimental details of the gel permeation chromatography work are given in Sections 6 and 7. This includes details about Sephadex gel swelling, column packing, chromatography, and detection.

TOC Detection

In the majority of the gel permeation chromatography work, detection was done by total organic carbon (TOC) analysis. Calibration of the TOC analyzer was done with solutions of potassium hydrogen phthalate. The calibration range and sample size were both dependent on the TOC content of the sample.

Chromatography and Data Transformation

The initial results of the Section 7 GPC experiments were TOC readings and corresponding sample times, which were entered into a Lotus 123 spreadsheet for transformation and chromatogram plotting. The formulas used in this spreadsheet and instuctions for their use, are given in Appendix 11. Sample time readings were converted to the cumulative time since sample injection. Chromatograms were converted from an x-axis time scale to a relative retention volume scale, as stated in Section 6.

The baselines were adjusted as follows. The baseline before elution of any effluent was adjusted to zero TOC by adding or subtracting from all readings the average background TOC before effluent elution. Next, the final baseline was adjusted to zero. This was done by addition or subtraction of a linear ramp which extended from the initial zeroed baseline to the baseline after elution. Due to possible adsorption of lipophilic effluent material in some effluents, it was common to experience a higher baseline after effluent elution than before.

The area under each chromatogram was next determined by integration, and the areas of all curves normalized to 1000 μg TOC. The normalization was done by setting the area of each curve equal to 1000 times the reciprocal of the integrated area.

The results of this transformation were normalized gel permeation chromatograms, on a relative retention volume scale. All of these chromatograms are presented in Appendix 12. The D or C stage effluent distributions appear in Appendix 12A and the (EO) stage effluent distributions appear in Appendix 12B. Under each set of process conditions (indicated on the chromatograms) one chromatogram for each of the 2 replicate effluents was run. The solid and dashed lines each present the chromatogram of a different effluent produced under the same bleaching conditions. It is from these chromatograms that the cumulative distributions given in Section 7 were made.

Statistical Analysis of Results

Analysis of variance (using NCSS statistical software) was performed on the percentage of effluent material with a molecular weight less than 1000, as explained in Section 7. Results of the analysis for the 8 different bleaching sequences and for the C or D and (EO) stage effluents, are given in Appendix 9G. Analysis was done on the mass of TOC (out of a total of 1000 μg) corresponding to a molecular weight of less than 1000.

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APPENDIX 1: CHARACTERIZATION OF EFFLUENT FRACTIONS FROM ClO_2 AND Cl_2 BLEACHING OF UNBLEACHED AND O_2 BLEACHED SOFTWOOD KRAFT PULPS (1993 TAPPI PULPING CONFERENCE VERSION)

A condensed version of this paper appears in Section 3. This more complete version is included because it contains data for all effluent fractions.

CHARACTERIZATION OF EFFLUENT FRACTIONS FROM ClO_2 AND Cl_2 BLEACHING OF UNBLEACHED AND O_2 BLEACHED SOFTWOOD KRAFT PULPS

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ABSTRACT

Effluents from OC(EO), OD(EO), and D(EO) laboratory bleaching of softwood kraft pulp were characterized by fractionation and analysis of the fractions. Adsorbable organic halide (AOX) and total organic carbon (TOC) were determined for the effluents and effluent fractions from each stage, with the exception of the oxygen stage. Each fraction was characterized in terms of its size, and in terms of its ratio of chlorine to carbon - an environmentally significant parameter. The fractionation consisted of ether extraction followed by separation of the extract into acidic, phenolic, and neutral subfractions.

Replacement of chlorine with chlorine dioxide after oxygen bleaching sharply reduced the AOX, TOC, and chlorine to carbon ratio (expressed as the number of chlorine atoms per 100 carbon atoms, Cl/C_{100}) of the whole effluents. Larger AOX and TOC reductions were seen in the ether soluble fraction and in the phenolic subfraction of the ether soluble material. Since both Cl/C_{100} and the size of the ether soluble fractions may be expected to correlate with the potential of an effluent for negative environmental effects, these observations show that replacement of chlorine by chlorine dioxide may be more beneficial than the resulting reductions in whole effluent AOX would suggest.

Oxygen delignification prior to a 100% chlorine dioxide stage reduced whole effluent AOX and TOC in rough proportion to the amount of lignin removed in the oxygen stage, but did not affect the overall Cl/C_{100}. The reductions in AOX and TOC in the environmentally significant ether soluble neutral and phenolic fractions were slightly larger. There was also a significant reduction in Cl/C_{100} in these fractions. Oxygen delignification, like chlorine dioxide substitution, may therefore be more beneficial than the overall AOX reduction would suggest.

INTRODUCTION

During the past decade, the possibility that pulp bleaching effluents may harm the environment has become a major issue with environmentalists and the general public alike. Total chlorinated organic material (measured as AOX) is currently of considerable interest. In fact, environmental pressures have led to either proposed or implemented AOX limits in several European countries and Canadian provinces (1, 2). Similar limits are likely in the U. S.

AOX regulation, together with the consumer's desire to buy "environmentally friendly" products, has led pulp mills to implement AOX reduction strategies. The AOX in pulp bleaching effluents may be decreased by one or more of the following process changes: improved brownstock washing (3-5), extended kraft delignification (6-8), O_2 delignification (3, 6, 9, 10), substitution of chlorine dioxide for chlorine (6, 9, 11-16), and oxidative caustic extraction (11, 17-19).

Although process changes can reduce the AOX, their effect on the environment remains uncertain since AOX reduction does not necessarily imply environmental impact reduction (20, 21). Because much of the effluent AOX is believed to be innocuous and only a small fraction potentially harmful, reducing the overall AOX may or may not reduce its environmental effects. The small, potentially harmful fraction is of low molecular weight and consists of hundreds or perhaps thousands of compounds, including certain environmentally troublesome ones. Such compounds or groups of them have been isolated and identified in pulp bleaching effluents. These include chlorophenolics (12, 16, 22-28), chlorinated dioxins (12, 25, 29), chlorinated neutral compounds (28, 30, 31), chlorinated carboxylic acids (28, 32) and chloroform (23, 33).

The complexity of pulp bleaching effluents complicates the task of developing a bleaching process that eliminates the potential for harmful effects on the environment. In an ideal world, a full chemical characterization would be done on effluents from a variety of process alternatives, and data on the environmental effects of each component would be available. It would

then be a simple task to choose the alternative that results in minimum environmental effect. Effluents are, however, sufficiently complex to defy full chemical characterization. For example, the toxicity of effluents can only be partially accounted for by identified components (24).

A practical alternative to the impossible ideal of complete analysis, is fractionation of the effluents from candidate bleaching processes and characterization of the fractions in terms that will allow prediction of environmental effects. Such an approach was adopted in the present study. Fractionation was conducted on the basis of ether solubility, volatility and acidity, and the fractions were characterized in terms of their relative amounts and chlorine to carbon ratios. Ether solubility implies low molecular weight (34, 35) and low molecular weight material may be correlated with acute and chronic toxicity (21, 36). The ether extract contains most of the effluent's mutagenicity (30, 37, 38) and toxicity (34). For example, Dence and co-workers (34) found that 92% of the C stage toxicity and 75% of the E stage toxicity resides in the corresponding ether extracts. Furthermore, the toxicities of the extracts were concentrated in the phenolic and neutral subfractions. The amounts of these subfractions therefore assume corresponding significance. The chlorine to carbon ratio may be used as a predictor of toxicity (24, 39) and lipophilicity (40).

EXPERIMENTAL APPROACH

Pulp Bleaching

Three different pulp bleaching sequences were considered in this work: OC(EO), OD(EO), and D(EO). The unbleached pulp was a mill produced kraft with a kappa number of 26.0 before the oxygen stage. The oxygen bleached pulp (kappa 14.1) was collected after the oxygen stage at the same mill. Kappa numbers after bleaching are given in Table I. Only the first two stages of pulp bleaching were done, since they effect the majority of the delignification, and therefore produce most of the effluent load. The D and C stages (referred to collectively as D/C stages throughout this report) were done in a batch reactor at 2% consistency, at 45°C, for 30 minutes, and with a kappa factor of 0.25; the (EO) stages were done in a high shear mixer at 10% consistency, at 70°C, and for 70 minutes.

Effluent Fractionation and Characterization

For the reasons mentioned above, effluent characterization was based on ether extraction. The ether extractable material was further separated into an acidic fraction, a phenolic fraction, and a neutral fraction. This type of procedure has been used in previous studies of mutagenicity (38, 41) and toxicity (34), and analyses of chlorophenols (26, 39), chlorinated neutral compounds (31, 42), and chlorinated carboxylic acids (32).

The TOC-normalized AOX, expressed as organically bound chlorine atoms per hundred carbon atoms (Cl/C_{100}), was determined for each effluent and effluent fraction. To measure Cl/C_{100} on the ether extract and extract fractions, the ether was first completely removed, then AOX and TOC measured on each fraction. The removal of ether was accomplished by evaporation of the sample to dryness or very near to dryness. During this process, other volatiles were also removed. To obtain information on the volatile fraction, a sample of the whole effluent was similarly evaporated and the carbon and chlorine losses determined.

Figure 1 depicts the effluent fractionation scheme, and Table II lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted exhaustively with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions: a non-extractable fraction, and two ether extractable fractions. The first ether fraction is material readily extracted and the second is removed slowly over an extended period. The first was further fractionated into acids, phenolics, and neutrals. Each fraction was then evaporated, as represented in Figure 1 by the dashed horizontal lines, to yield the final samples.

Data Analysis

All bleaching sequences were performed in duplicate, and the individual stage effluents from each replication were fractionated and analyzed separately. This resulted in two completely independent sets of data for each sequence. The D/C and (EO) stage data for all fractions are given in Tables III-X. The total TOC and AOX (given in Table III) represents TOC and AOX mass balances around the fractionation scheme and were determined as the sums of the AOX and TOC determinations of the neutrals, the phenolics, the

acids, the polar fraction, the hydrophilic fraction, and the volatiles.

In this report emphasis will be placed on the whole effluents and on the ether soluble fraction, the phenolics, and the neutrals, since evidence in the literature indicates these fractions may be more environmentally important than the others. The Cl/C_{100} and the percentage of total TOC are also emphasized, since all needed information can be gained from these two results. The Cl/C_{100} gives an estimate of the relative environmental behavior of the material, and the percentage of the total TOC gives a measure of the total amount of material. The percentage of total TOC is used in order to normalize the TOC data for different levels of removed material.

Analyses of variance (AOV) were done on the data from each fraction, to assess the significance of differences between sequences and between stages. Since data with high Cl/C_{100} clearly had a greater variance than the low Cl/C_{100} data, all Cl/C_{100} data were log transformed to stabilize variance. When AOV showed a significant effect between bleaching sequences, least significant differences were determined using Duncan's multiple range test (43).

RESULTS AND DISCUSSION

Whole Effluents

Data for the whole effluents are presented in Table III. The whole effluents contain 3.8-17 kg/t TOC and 0.1-2.8 kg/t AOX, depending on the stage and sequence.

Figure 2 compares the three partial bleaching sequences with respect to mean TOC production. TOC provides a measure of the total organic load produced by each sequence. As expected, based on the higher pulp kappa number entering the sequence, the D(EO) sequence produces the greatest quantity of TOC. In the case of the oxygen based sequences about half of the organic material has already been removed in the oxygen stage prior to delignification with chlorine based chemicals. This material is recycled to the mill's recovery system and is therefore without environmental significance in the wastewater stream.

A comparison of the oxygen based sequences shows that chlorine produces more TOC than chlorine dioxide in both the D/C and (EO) stages. This is in part due to the more effective delignification done by chlorine, but the difference is too great to be due to this effect alone. The data suggest that the OD(EO) sequence gives a higher carbohydrate yield. This is discussed further below.

Figure 3 presents a similar comparison of mean Cl/C_{100}. In both stages the material released by chlorine bleaching is much more extensively chlorinated than that released by chlorine dioxide bleaching. This is expected since chlorine reacts by both oxidation and substitution while chlorine dioxide only reacts by oxidation (44, 45). The ClO_2 bleaching produces some chlorinated organics as well, as a result of the formation and reaction of HOCl and Cl_2 during the process (46-48).

Insertion of an O_2 stage before ClO_2 has little effect on the extent of chlorination of effluent compounds, although some decrease is seen in the case of the (EO) stage effluents. This may be a result of the action of O_2 delignification. Oxygen in alkaline solution oxidizes free phenolic structures (44, 49), thus reducing the number of sites that are readily substituted by chlorine. Another possible explanation is that material from the OD(EO) sequence is more readily dechlorinated in the caustic extraction stage than that material from the D(EO) sequence.

Ether Soluble Fraction

Table IV presents detailed data for the ether soluble fraction. This fraction contains 0.3-1.4 kg/t TOC, representing 4-13% of the total TOC and 0.01-0.79 kg/t AOX, representing 7-35% of the total AOX. A change from chlorine to chlorine dioxide bleaching reduces both TOC and AOX in this fraction to a greater extent than occurs in the whole effluent.

Figure 4 presents the mean ether soluble TOC as a percentage of total TOC for each bleaching sequence. For both the D/C and (EO) stages, chlorine results in a higher ether soluble TOC content than chlorine dioxide. The D(EO) sequence has a smaller percentage of total TOC in this fraction than OD(EO). Because of the increased lignin removal however, the absolute amounts of removed AOX and TOC in this fraction are greater for D(EO).

Figure 5 similarly compares the sequences with regard to Cl/C_{100}. For both the D/C and (EO) stages, this fraction contains increased chlorine per unit carbon compared to the whole effluents. This further supports the contention that the ether soluble fraction is of environmental interest. The ether soluble fraction is

also chlorinated to a much greater extent when chlorine is used rather than chlorine dioxide. In fact the increased degree of chlorine substitution on the organic material in the case of chlorine results in a more hydrophobic effluent and is the likely cause of the increased ether soluble TOC that is also seen when chlorine is used. Use of chlorine dioxide provides two environmental benefits over chlorine use, in the case of the ether soluble material: a large reduction in the amount of organically bound chlorine per unit carbon, and a reduced amount of material within the fraction. There is no significant Cl/C_{100} effect seen between the OD(EO) and D(EO) sequences.

Phenolic Fraction

Detailed results of analysis of the phenolic fraction are shown in Table V. The phenolic fraction contains 0.02-0.12 kg/t TOC or 0.5-1.5% of the total TOC, and 0.002-0.09 kg/t AOX or 0.8-4.1% of the total AOX. Both TOC and AOX are again reduced to a greater extent in this fraction than in the whole effluent, when the change is made from chlorine to chlorine dioxide bleaching.

Figure 6 compares the phenolic TOC as a percentage of total TOC for the three sequences. Chlorine bleaching results in an increased content of phenolic TOC relative to chlorine dioxide for both the D/C and (EO) stages. The reduced amount of phenolic material with ClO_2 bleaching is in accordance with other studies in which the amount of measured chlorophenolics decreased as ClO_2 substitution increased (22, 24, 28, 50).

Figure 7 compares the phenolic fraction Cl/C_{100} for the three bleaching sequences and for both stages. Chlorine produces a much more extensively chlorinated phenolic fraction than does chlorine dioxide. The two benefits from the use of chlorine dioxide rather than chlorine are again seen here: decreased phenolic AOX per unit carbon, as well as a decreased amount of material in the phenolic fraction.

No significant differences were seen between the OD(EO) and D(EO) sequences by the normal AOV. However if only the OD(EO) and D(EO) data are included in the analysis, a significantly greater Cl/C_{100} is seen for D(EO) bleaching compared to OD(EO).

Neutral Fraction

Complete data on the neutral fraction are shown in Table VI. The fraction contains 0.05-0.14 kg/t TOC (0.4-1.2% of the total TOC) and 0.001-0.006 kg/t AOX (0.3-1.4% of the total AOX).

Figure 8 compares the bleaching sequences with regard to neutral fraction TOC as a percentage of the total TOC. There are no statistically significant differences between any of the bleaching sequences, due to scatter in the replicate data.

Figure 9 compares the neutral fraction Cl/C_{100} for the sequences. Again chlorine produces a more highly chlorinated material than does chlorine dioxide, for both D/C and (EO) stages. The D(EO) sequence also produces a more highly chlorinated material than the OD(EO) sequence. This is another indication that oxygen delignification leaves a residual lignin that is less susceptible to chlorine substitution reactions than unoxidized lignin.

Acid Fraction

Table VII presents the detailed results for the acid fraction of the ether soluble material. About 0.2-1.1 kg/t TOC, representing 3-10% of the total TOC and 0.01-0.46 kg/t AOX, representing 6-20% of the total AOX, is contained within this fraction.

Figures 10 and 11 show the acid fraction TOC as a percent of the total, and the acid fraction Cl/C_{100}. Replacement of chlorine with chlorine dioxide results in a decreased percentage of total TOC in the (EO) stage fraction and reduces the Cl/C_{100} for both stages. Oxygen bleaching prior to chlorine dioxide treatment results in a decreased Cl/C_{100} for the (EO) stage fraction, but an increased percentage of TOC in the fraction for both stages. The absolute amounts of TOC and AOX in the acid fraction are again greater for D(EO) bleaching, however.

Polar Fraction

Complete data for the polar fraction, or difficultly ether extractable material, are shown in Table VIII. The fraction contains 0.2-1.1 kg/t TOC or 3-11% of total TOC, and 0.003-0.09 kg/t AOX or 2-20% of the total AOX.

Figures 12 and 13 show the mean polar fraction data for both percent of total TOC and Cl/C_{100}. A change from chlorine to chlorine dioxide use results in a decreased (EO) stage Cl/C_{100} for the fraction. The presence of oxygen bleaching before ClO_2 treatment results in an increased D/C stage Cl/C_{100} but a decrease

in the percentage of the total TOC within the D/C stage polar fraction. A decreased (EO) stage Cl/C_{100} is also seen when O_2 bleaching precedes ClO_2 treatment.

Hydrophilic Fraction

Table IX presents the entire data set for the hydrophilic fraction or the non-extractable material. The hydrophilic fraction contains 3.4-13.4 kg/t TOC (68-86% of the total TOC) and 0.07-1.4 kg/t AOX (49-85% of the total AOX).

Figures 14 and 15 show the hydrophilic TOC as a percent of the total TOC, and the hydrophilic fraction Cl/C_{100} for the bleaching sequences. The Cl/C_{100} values for this fraction are similar to those found for "high molecular weight" effluent material in other studies (28, 49, 51, 52). Although there may appear to be differences between the sequences in Figure 14, the percentage of total TOC does not differ significantly. This again is due to scatter in the replicate data. The use of chlorine dioxide in place of chlorine causes a reduced Cl/C_{100} for both stages, and the presence of oxygen bleaching before chlorine dioxide treatment reduces the Cl/C_{100} for both stages as well.

Volatile Fraction

The data set for the volatile fraction is shown in Table X. About 0.3-1.1 kg/t TOC or 4-16% of the total TOC, and 0.005-0.3 kg/t or 1.5-18% of the total AOX is volatile material. Figures 16 and 17 show the mean data for the percent of total TOC and Cl/C_{100}. There are no statistically significant differences, due to scatter in the replicate data.

Yield Implications of Whole Effluent TOC

A summary of the TOC removed in both the D/C and (EO) stages, the CE kappa numbers, the kappa change brought about by the bleaching sequence, and the ratio of TOC to the change in kappa number is shown for each bleaching sequence in Table I. Analysis of variance on the ratio of TOC to kappa change showed that the effluents from pulp chlorination contained significantly more TOC per unit of kappa number reduction than either chlorine dioxide case.

The increased amount of TOC in the effluent per unit of kappa loss implies greater carbohydrate loss, or reduced pulp yield with 100% chlorine as compared to 100% chlorine dioxide. In a review of pulp yield data at different levels of ClO_2 substitution, increased yield was seen in 40°C stages at increased ClO_2 substitution, while no such yield increases were seen at lower temperatures (53). This work, in which D/C stages were done at 45°C, is consistent with those results.

Another possible explanation for the decreased TOC per unit kappa number decrease seen with chlorine dioxide bleaching, is formation of carbonate species during bleaching. Such species are evolved as CO_2, and not measured as TOC.

EXPERIMENTAL METHODS

Pulp Bleaching

Two pulp samples were used in these experiments: a 26.0 kappa unbleached southern softwood and a 14.1 kappa O_2 delignified southern softwood. Both pulps were produced at the same mill. The unbleached pulp was collected just before the O_2 stage, and the O_2 delignified pulp was collected just after the O_2 stage. Each pulp was well washed before bleaching.

D/C Stages.

All D/C stages were done in a 20L batch reactor, designed to rapidly add bleaching chemicals. Bleaching was done at 2% consistency, at 45°C, for 30 minutes, and at a kappa factor of 0.25. The mixer was run at 350 rpm. Initial pH in all cases was adjusted to 2 by the addition of sulfuric acid solution.

(EO) Stages.

All (EO) stages were done in a Quantum Technologies high shear mixer at 10% consistency, at 70°C, and for 70 minutes. The NaOH charge was 0.55 X TAC, the O_2 charge was 0.5% on pulp, and 4.1% of the total D/C stage filtrate was included as carryover. The slurry was mixed at 15 Hertz for 3 seconds, every 5 minutes.

Effluent Preparation

The D/C stage effluent was collected by filtration of the 2% slurry; the (EO) stage effluent was similarly collected after the 10% slurry was diluted to 2%. This was done to maintain a similar TOC content in all effluents for ether extraction. Effluent samples were filtered to remove any fibers, quenched with excess Na_2SO_3, and acidified to a pH of less than 2. Ether ex-

tractions were always started within 2 days of effluent collection.

Ether Extraction of Effluents

Ether extraction was done on 4L of effluent using continuous liquid-liquid extractors. Extraction was carried out with 500 ml of diethyl ether. The first ether phase was collected after 96 hours of extraction and was replaced with 500 ml of fresh ether. Extraction was continued for 336 total hours. The extraction was then stopped and the second ether phase and the non-extractable materials were collected.

Ether Extract Fractionation

The first ether phase was diluted to 500 ml, 100 ml of the sample collected, and the remaining ether placed in a separatory funnel for fractionation. The ether was extracted 3 times with 25 ml of 0.5 M $NaHCO_3$, and the extracts collected and acidified. The ether was next extracted 3 times with 25 ml of 0.5 M NaOH, and these extracts also collected and acidified. The $NaHCO_3$ soluble material is the acidic fraction, the NaOH soluble material is the phenolic fraction, and the remaining ether soluble material is the neutral fraction.

Sample Preparation

Ether was removed from all samples by evaporation to dryness, or near to dryness. The samples were then dissolved in water, acidified, and diluted to a known volume. To ensure reasonable sample recovery and to be certain the ether was removed, TOC and AOX mass balances were done around the fractionation scheme.

TOC Analysis

Measurement of TOC was done on a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate. Samples were prepared for TOC analysis by acidifying them, and sparging for 5 minutes with nitrogen to drive off any interfering carbonate species.

AOX Analysis

Measurement of AOX was done on a Dohrman model DX-20 organic halide analyzer. Sample preparation was done by a slight modification of method SCAN-W 9:89 (54). In this case samples were shaken for 4 hours rather one, to more completely adsorb the polar fractions.

SUMMARY AND CONCLUSIONS

Figures 18 and 19 summarize the total D/C + (EO) stage TOC and AOX for the bleaching sequences. The size of each graph is proportional to the TOC or AOX (in kg/t) produced in the corresponding bleaching sequence. Figure 18 shows that D(EO) bleaching produces the most effluent TOC, as expected based on the higher kappa number of the pulp. The OC(EO) sequence produces more effluent TOC than OD(EO) because of both the greater delignification effectiveness of chlorine and possible increased carbohydrate loss. As shown in Figure 19, the OD(EO) sequence results in only a small fraction of the total AOX produced by the OC(EO) sequence. The AOX in the effluent fractions is also smaller by a corresponding amount. As expected, the D(EO) sequence produces about twice the AOX as the OD(EO) sequence.

Certain significant conclusions regarding the nature of bleaching effluents produced by both chlorine and chlorine dioxide bleaching can be based on this research. For the whole effluents, chlorine bleaching gives a higher Cl/C_{100} than ClO_2 bleaching of the same pulp. The same trend is seen for effluent fractions which are environmentally significant. In the case of the ether soluble fraction and the phenolic fraction, not only is the Cl/C_{100} greater for Cl_2 bleaching, but a greater percentage of the total TOC partitions into the ether soluble and phenolic fractions as well. The phenolic and neutral fractions for both the D/C and (EO) stages have lower Cl/C_{100} values when oxygen bleaching precedes chlorine dioxide treatment.

The results of this research provide some new evidence in support of the use of chlorine dioxide and O_2 delignification as a means of environmental improvement. By using ClO_2 in place of Cl_2, not only is the amount of chlorine substitution on organic compounds greatly reduced, but the percentage of material within certain environmentally important fractions is also reduced. Oxygen bleaching, in addition to the expected benefit of reducing in half the total effluent load, provides a decreased level of chlorine substitution of organic compounds in the phenolic and neutral fractions of both D/C and (EO) stage effluents. Therefore, both chlorine dioxide substitution and oxygen bleaching may be more environmentally beneficial than the overall AOX reduction suggests.

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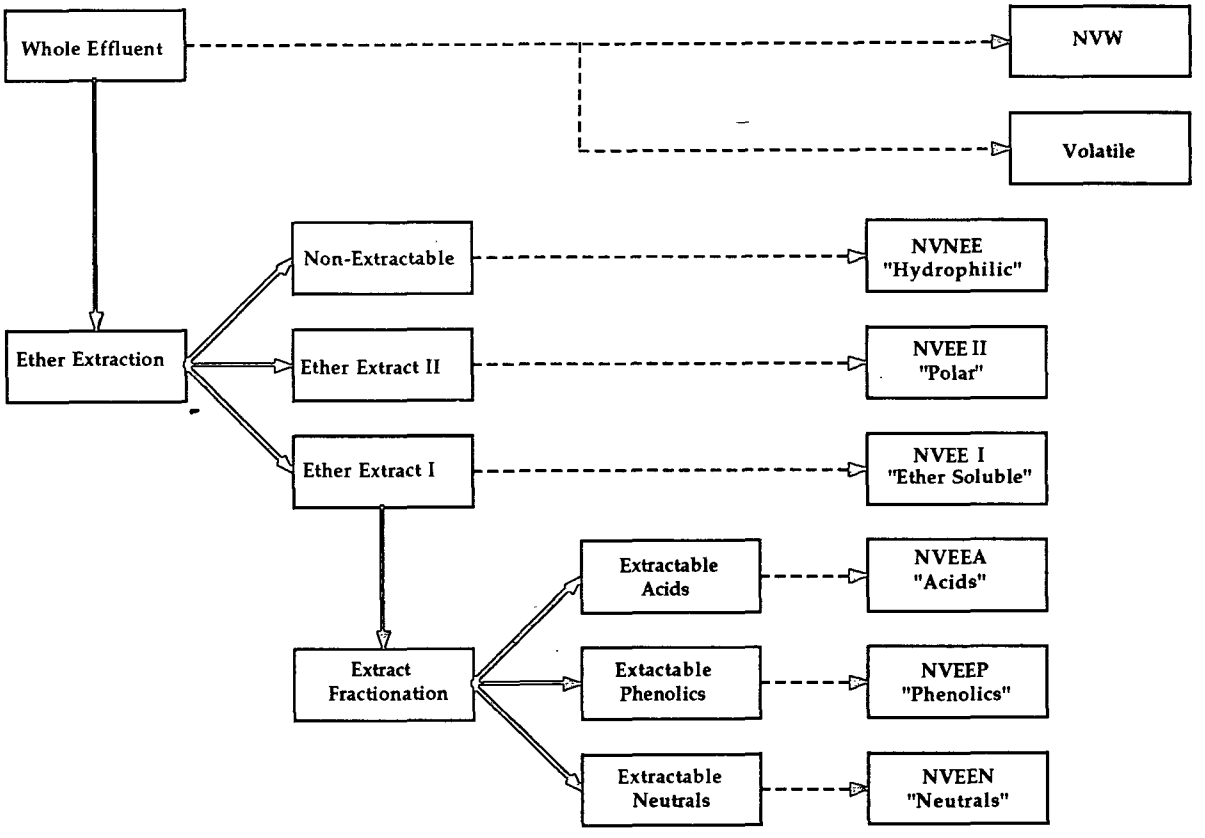
Figure 1. Effluent Fractionation.



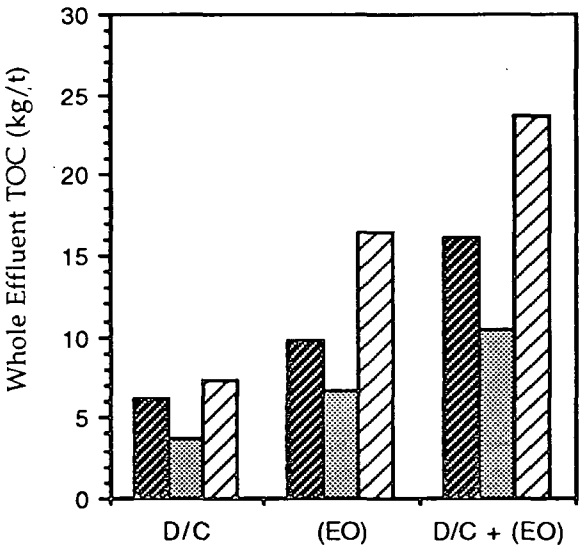


Figure 2. Whole Effluent TOC.

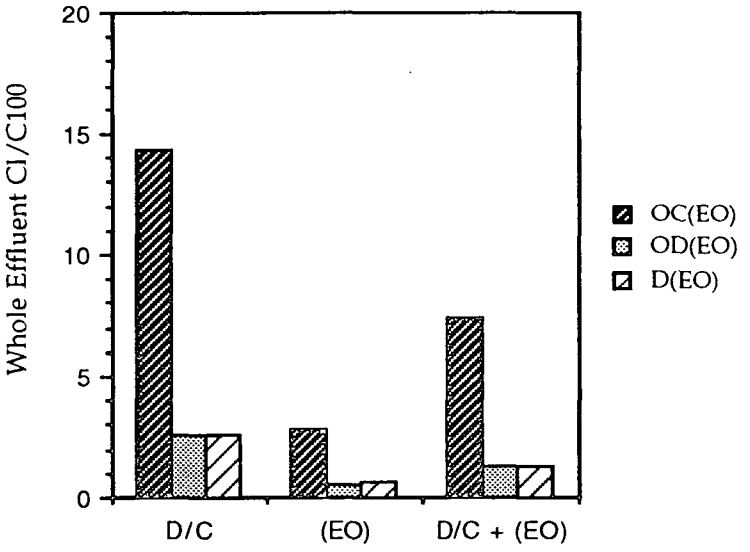


Figure 3. Whole Effluent Cl/C100.

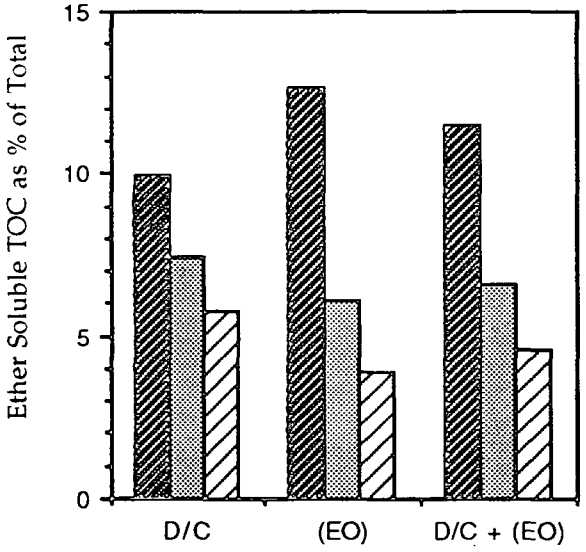
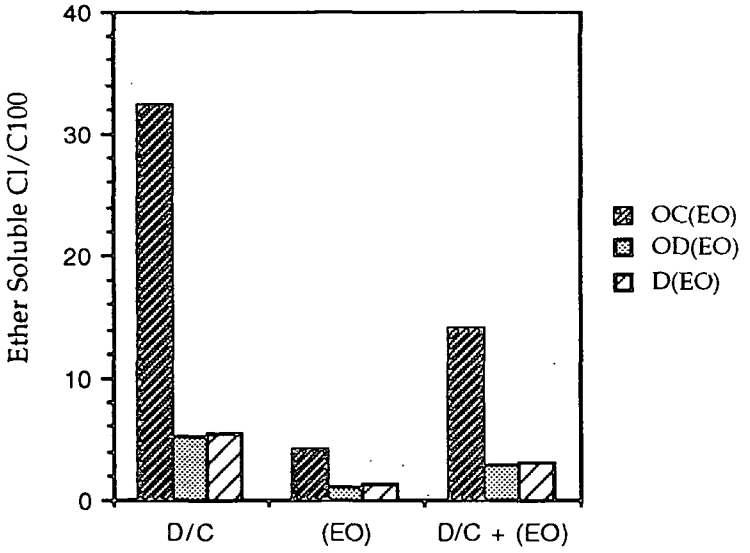


Figure 4. Ether Soluble TOC as % of Total.



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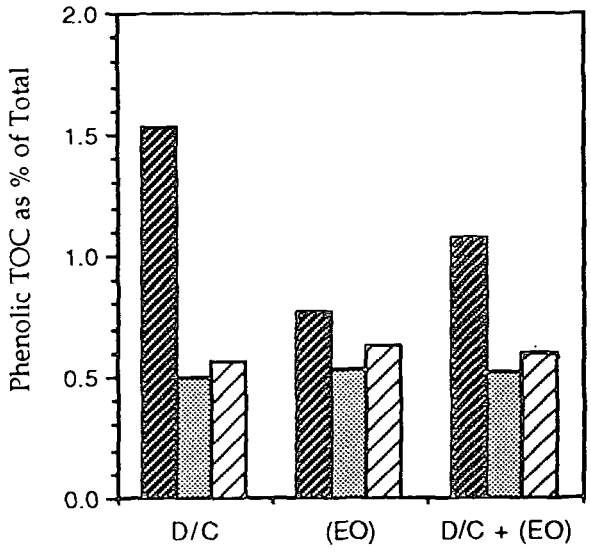

Figure 6. Phenolic TOC as % of Total.

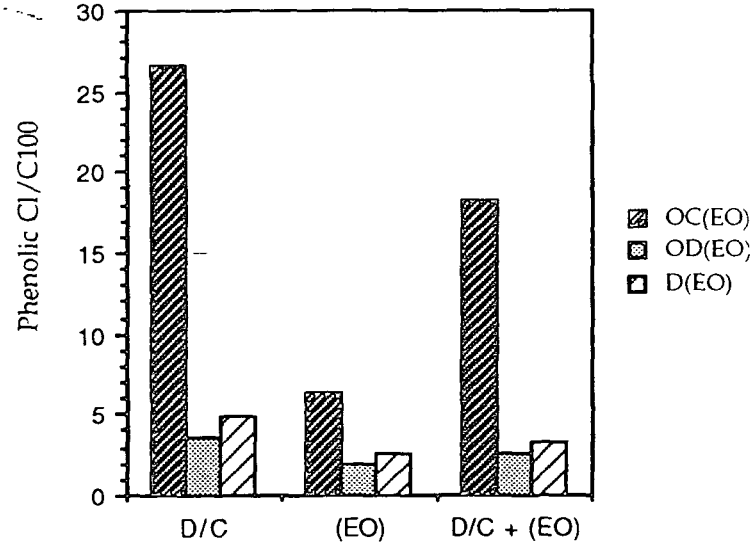

Figure 7. Phenolic Cl/C100.

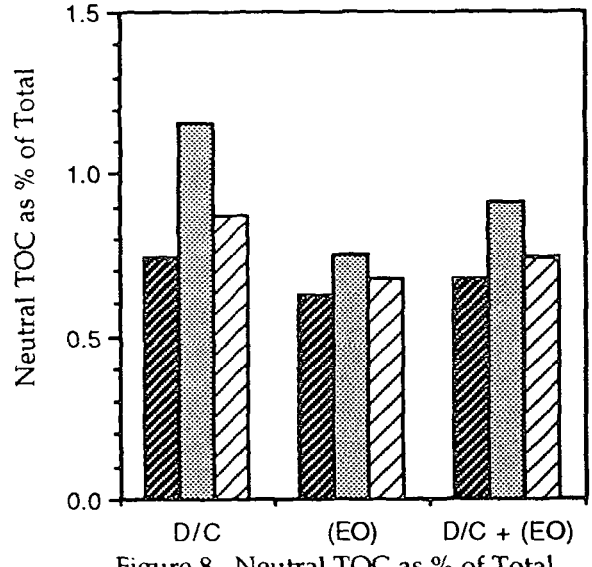

Figure 8. Neutral TOC as % of Total.

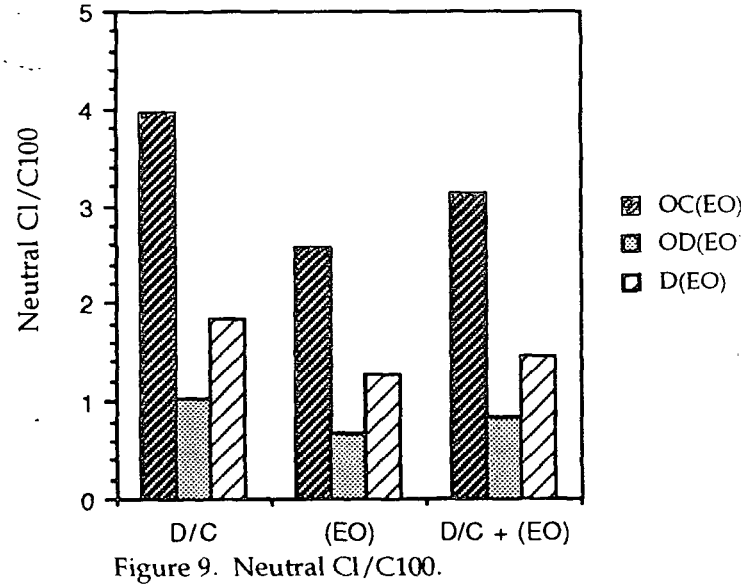

Figure 9. Neutral Cl/C100.

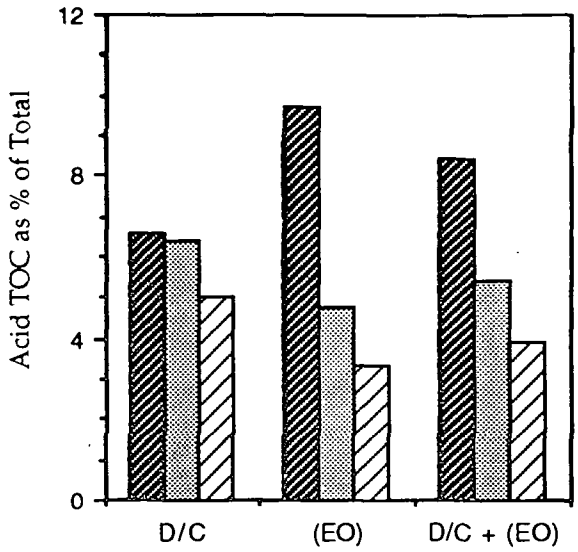

Figure 10. Acid TOC as % of Total.

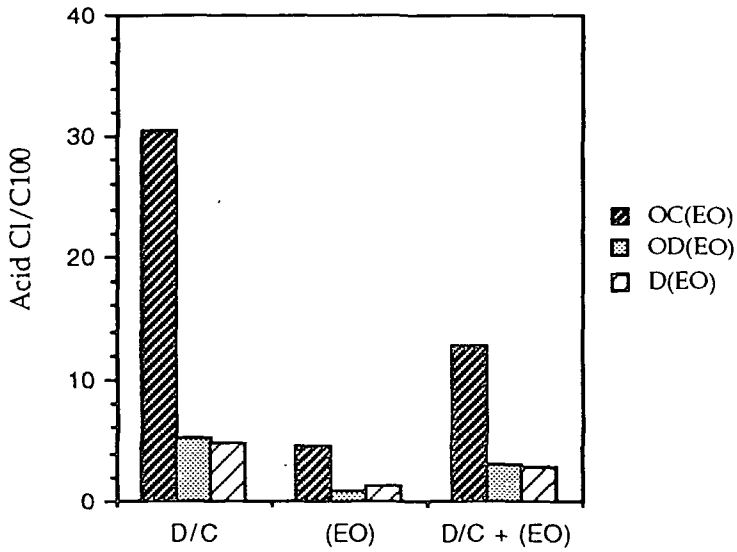

Figure 11. Acid Cl/C100.

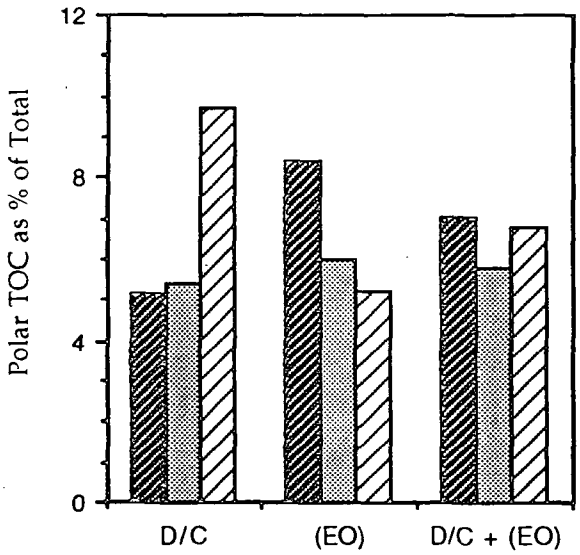

Figure 12. Polar TOC as % of Total.

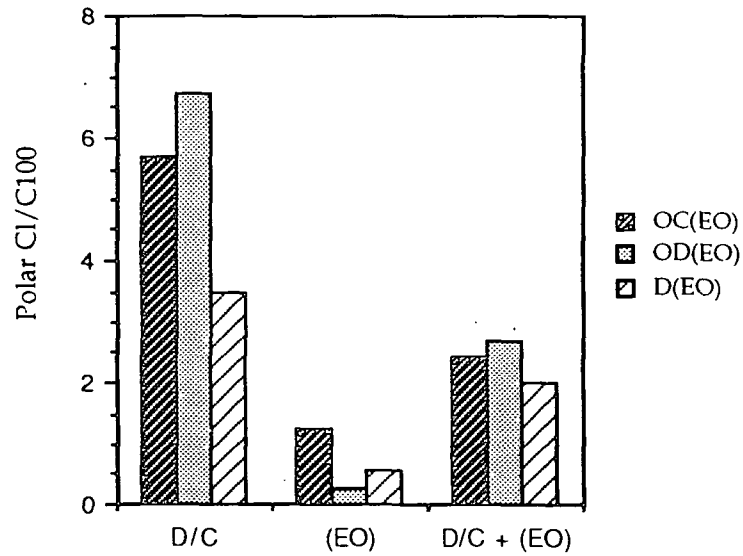

Figure 13. Polar Cl/C100.

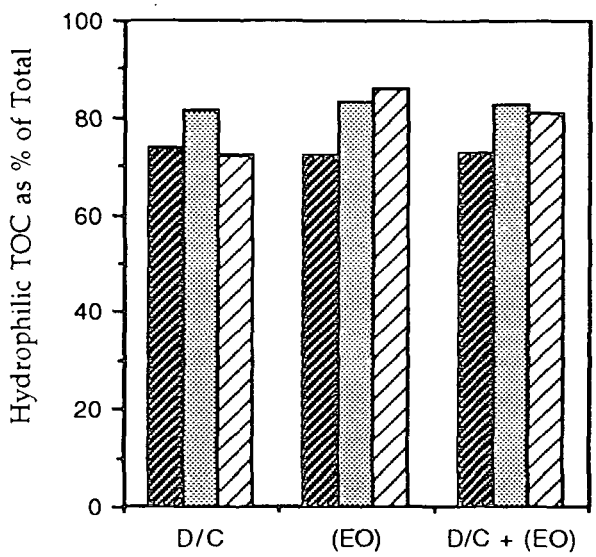

Figure 14. Hydrophilic TOC as % of Total.

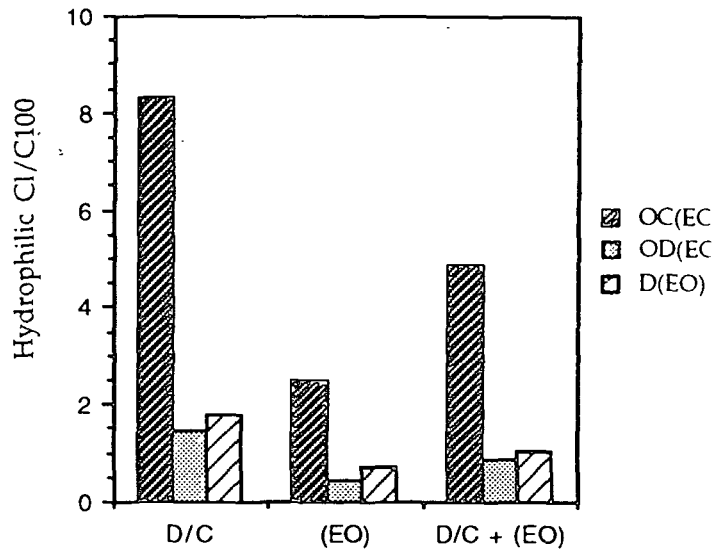

Figure 15. Hydrophilic Cl/C100.

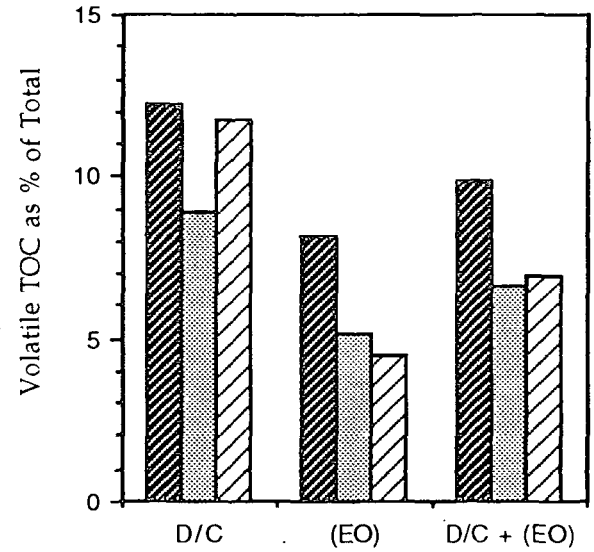

Figure 16. Volatile TOC as % of Total.

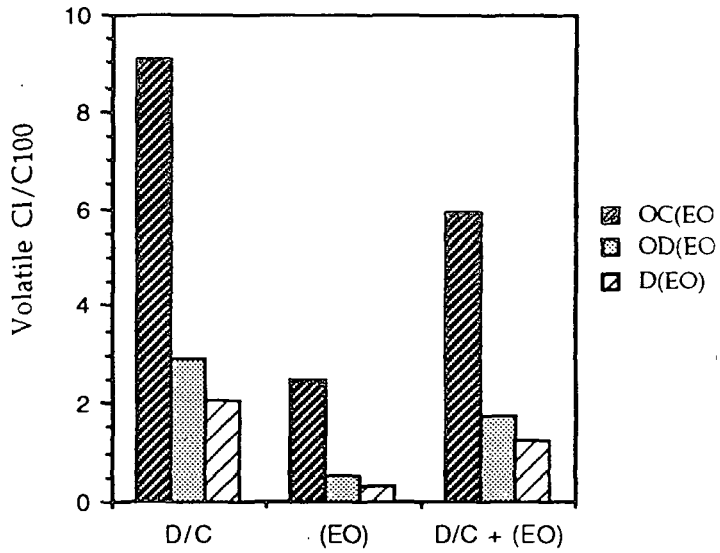

Figure 17. Volatile Cl/C100.

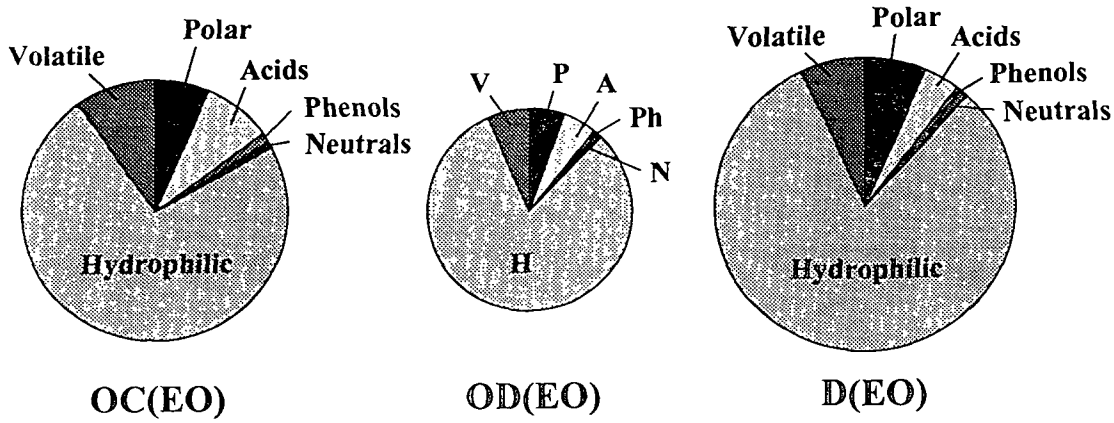

Figure 18. TOC Summary Graphs.

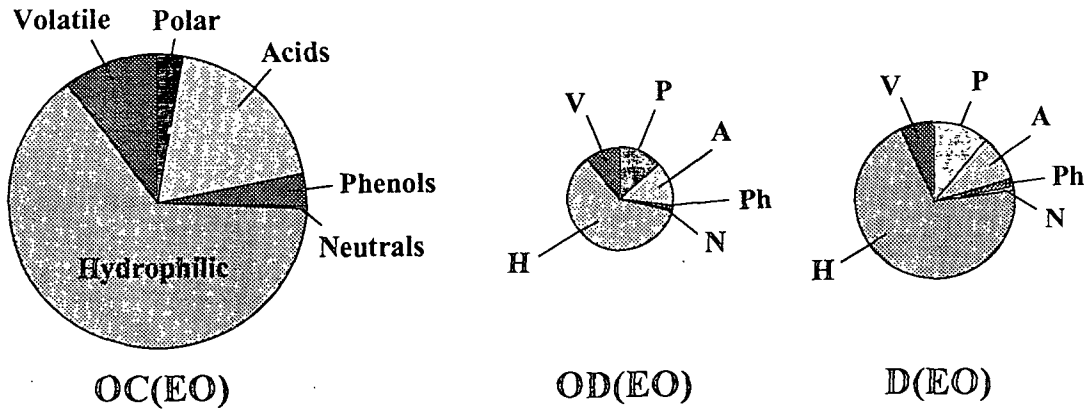

Figure 19. AOX Summary Graphs.

Table I. D/C + (EO) TOC and CE Kappa Number Data.

Sequence	D/C + (EO) TOC (kg/t)	CE kappa	Δ kappa	TOC/Δ kappa
OC(EO)	16.6	2.10	12.0	1.38
OC(EO)	15.5	1.74	12.4	1.26
OD(EO)	10.6	4.23	9.87	1.08
OD(EO)	10.4	4.44	9.66	1.08
D(EO)	24.4	5.27	20.7	1.18
D(EO)	22.9	4.83	21.2	1.08

Table II. Effluent Fraction Codes and Descriptions of Fractions.

Fraction Code	Description
NVW	Non-volatile, whole.
NVNEE	Non-volatile, not extracted with ether ("Hydrophilic").
NVEE II	Non-volatile, difficult to extract with ether ("Polar").
NVEE I	Non-volatile, readily ether extractable ("Ether Soluble").
NVEEA	Non-volatile, ether extractable acidic compounds ("Acids").
NVEEP	Non-volatile, ether extractable phenolic compounds ("Phenolics").
NVEEN	Non-volatile, ether extractable neutral compounds ("Neutrals").

Table III. Whole Effluent.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	6.15	6.36	3.85	3.80	7.33	7.23
Total TOC, kg/t	7.03	8.17	4.43	4.29	7.87	8.02
AOX, kg/t	2.75	2.56	0.299	0.294	0.552	0.594
Total AOX, kg/t	2.26	2.13	0.297	0.264	0.447	0.551
Cl/C_{100}	15.1	13.6	2.63	2.61	2.54	2.78

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	9.37	10.2	6.79	6.60	17.1	15.7
Total TOC, kg/t	9.83	11.6	6.70	6.52	15.6	14.9
AOX, kg/t	0.793	0.858	0.101	0.102	0.341	0.309
Total AOX, kg/t	0.738	0.887	0.0938	0.0930	0.324	0.306
Cl/C_{100}	2.86	2.86	0.50	0.52	0.68	0.67

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	15.5	16.6	10.6	10.4	24.4	22.9
Total TOC, kg/t	16.9	19.8	11.1	10.8	23.5	22.9
AOX, kg/t	3.54	3.42	0.400	0.396	0.893	0.903
Total AOX, kg/t	3.00	3.02	0.391	0.357	0.771	0.857
Cl/C_{100}	7.71	6.98	1.27	1.29	1.24	1.33

Table IV. Ether Soluble Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.681	0.832	0.383	0.267	0.501	0.418
% of Total TOC	9.69	10.2	8.65	6.22	6.37	5.21
AOX, kg/t	0.790	0.632	0.0547	0.0439	0.0751	0.0725
% of Total AOX	35.0	29.7	18.4	16.6	16.8	13.2
Cl/C_{100}	39.2	25.6	4.83	5.56	5.05	5.88

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.32	1.36	0.406	0.399	0.663	0.542
% of Total TOC	13.4	11.7	6.06	6.12	4.25	3.64
AOX, kg/t	0.173	0.154	0.0127	0.0125	0.0273	0.0220
% of Total AOX	23.4	17.4	13.5	13.4	8.43	7.19
Cl/C_{100}	4.44	3.83	1.06	1.06	1.39	1.37

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	2.00	2.19	0.789	0.666	1.16	0.960
% of Total TOC	11.9	11.1	7.09	6.16	4.94	4.19
AOX, kg/t	0.963	0.786	0.0674	0.0564	0.102	0.0945
% of Total AOX	32.1	26.0	17.2	15.8	13.2	11.0
Cl/C_{100}	16.3	12.1	2.89	2.86	2.97	3.33

Table V. Phenolic Fraction.

D/C Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.108	0.123	0.0239	0.0198	0.0462	0.0434
% of Total TOC	1.54	1.51	0.54	0.46	0.59	0.54
AOX, kg/t	0.0935	0.0869	0.00255	0.00201	0.00683	0.00602
% of Total AOX	4.14	4.08	0.86	0.76	1.53	1.09
Cl/C_{100}	29.2	23.8	3.60	3.45	5.00	4.69
(EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.0884	0.0725	0.0364	0.0341	0.0820	0.107
% of Total TOC	0.90	0.63	0.54	0.52	0.53	0.72
AOX, kg/t	0.0221	0.00924	0.00243	0.00180	0.00697	0.00730
% of Total AOX	2.99	1.04	2.59	1.94	2.15	2.39
Cl/C_{100}	8.47	4.31	2.26	1.79	2.87	2.31
D/C + (EO) Stage	**OC(EO)**		**OD(EO)**		**D(EO)**	
TOC, kg/t	0.196	0.196	0.0603	0.0539	0.128	0.150
% of Total TOC	1.16	0.99	0.54	0.50	0.55	0.65
AOX, kg/t	0.116	0.0961	0.00498	0.00381	0.0138	0.0133
% of Total AOX	3.87	3.18	1.27	1.07	1.79	1.55
Cl/C_{100}	20.0	16.6	2.79	2.39	3.64	3.00

Table VI. Neutral Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.0393	0.0750	0.0551	0.0457	0.0784	0.0583
% of Total TOC	0.56	0.92	1.24	1.07	1.00	0.73
AOX, kg/t	0.00591	0.00629	0.00153	0.00148	0.00342	0.00387
% of Total AOX	0.26	0.30	0.52	0.56	0.77	0.70
Cl/C_{100}	5.08	2.83	0.94	1.09	1.48	2.24

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.0671	0.0676	0.0511	0.0480	0.0685	0.137
% of Total TOC	0.68	0.58	0.76	0.74	0.44	0.92
AOX, kg/t	0.00520	0.00513	0.00129	0.000701	0.00275	0.00495
% of Total AOX	0.71	0.58	1.38	0.75	0.85	1.62
Cl/C_{100}	2.62	2.56	0.85	0.49	1.36	1.22

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.106	0.143	0.106	0.0937	0.147	0.195
% of Total TOC	0.63	0.72	0.95	0.87	0.63	0.85
AOX, kg/t	0.0111	0.0114	0.00282	0.00218	0.00617	0.00882
% of Total AOX	0.37	0.38	0.72	0.61	0.80	1.03
Cl/C_{100}	3.54	2.69	0.90	0.79	1.42	1.53

Table VII. Acid Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.450	0.548	0.316	0.242	0.432	0.361
% of Total TOC	6.40	6.71	7.13	5.64	5.49	4.50
AOX, kg/t	0.456	0.430	0.0511	0.0369	0.0561	0.0535
% of Total AOX	20.2	20.2	17.2	14.0	12.6	9.71
Cl/C_{100}	34.2	26.5	5.46	5.15	4.39	5.00

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.02	1.05	0.304	0.321	0.526	0.491
% of Total TOC	10.4	9.05	4.54	4.92	3.37	3.30
AOX, kg/t	0.140	0.135	0.00856	0.00827	0.0192	0.0214
% of Total AOX	19.0	15.2	9.13	8.89	5.93	6.99
Cl/C_{100}	4.67	4.37	0.95	0.87	1.24	1.47

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.47	1.60	0.620	0.563	0.958	0.852
% of Total TOC	8.72	8.09	5.57	5.21	4.08	3.72
AOX, kg/t	0.596	0.565	0.0597	0.0452	0.0753	0.0749
% of Total AOX	19.9	18.7	15.3	12.7	9.77	8.74
Cl/C_{100}	13.7	11.9	3.25	2.71	2.66	2.97

Table VIII. Polar Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.533	0.220	0.226	0.248	0.829	0.719
% of Total TOC	7.58	2.69	5.10	5.78	10.5	8.97
AOX, kg/t	0.0632	0.0479	0.0445	0.0502	0.0882	0.0705
% of Total AOX	2.80	2.25	15.0	19.0	19.7	12.8
Cl/C_{100}	4.00	7.35	6.67	6.85	3.60	3.31

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.05	0.711	0.399	0.395	0.858	0.739
% of Total TOC	10.7	6.13	5.96	6.06	5.50	4.96
AOX, kg/t	0.0288	0.0325	0.00333	0.00280	0.0124	0.0136
% of Total AOX	3.90	3.66	3.55	3.01	3.83	4.44
Cl/C_{100}	0.93	1.55	0.28	0.24	0.49	0.62

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.58	0.931	0.625	0.643	1.69	1.46
% of Total TOC	9.39	4.71	5.62	5.95	7.19	6.36
AOX, kg/t	0.0920	0.0804	0.0478	0.0530	0.101	0.0841
% of Total AOX	3.07	2.66	12.2	14.8	13.1	9.81
Cl/C_{100}	1.97	2.92	2.59	2.79	2.02	1.95

Table IX. Hydrophilic Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	4.80	6.50	3.43	3.69	5.41	6.05
% of Total TOC	68.3	79.6	77.4	86.0	68.7	75.4
AOX, kg/t	1.34	1.37	0.144	0.160	0.278	0.333
% of Total AOX	59.3	64.3	48.5	60.6	62.2	60.4
Cl/C_{100}	9.52	7.09	1.42	1.47	1.74	1.86

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	6.67	8.88	5.50	5.45	13.4	12.7
% of Total TOC	67.9	76.6	82.1	83.6	85.9	85.2
AOX, kg/t	0.531	0.594	0.0728	0.0745	0.276	0.252
% of Total AOX	72.0	67.0	77.6	80.1	85.2	82.4
Cl/C_{100}	2.69	2.26	0.45	0.46	0.69	0.67

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	11.5	15.4	8.93	9.14	18.8	18.8
% of Total TOC	68.0	77.8	80.2	84.6	80.1	81.8
AOX, kg/t	1.87	1.96	0.217	0.235	0.554	0.585
% of Total AOX	62.3	64.9	55.5	65.8	71.9	68.3
Cl/C_{100}	5.51	4.31	0.82	0.87	1.00	1.05

Table X. Volatile Fraction.

D/C Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	1.11	0.700	0.380	0.396	1.07	0.785
% of Total TOC	15.8	8.57	8.58	9.23	13.6	9.79
AOX, kg/t	0.301	0.186	0.0533	0.0136	0.0141	0.0846
% of Total AOX	13.3	8.73	17.9	5.15	3.15	15.4
Cl/C_{100}	9.17	8.93	4.74	1.16	0.45	3.65

(EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	0.935	0.797	0.405	0.271	0.653	0.706
% of Total TOC	9.51	6.87	6.04	4.16	4.19	4.74
AOX, kg/t	0.0108	0.110	0.00539	0.00490	0.00661	0.00637
% of Total AOX	1.46	12.4	5.75	5.27	2.04	2.08
Cl/C_{100}	0.39	4.65	0.45	0.61	0.34	0.30

D/C + (EO) Stage	OC(EO)		OD(EO)		D(EO)	
TOC, kg/t	2.05	1.50	0.785	0.667	1.72	1.49
% of Total TOC	12.2	7.59	7.05	6.17	7.33	6.50
AOX, kg/t	0.312	0.296	0.0587	0.0185	0.0207	0.0910
% of Total AOX	10.4	9.80	15.0	5.18	2.68	10.6
Cl/C_{100}	5.14	6.67	2.53	0.94	0.41	2.06

APPENDIX 2: THE EFFECT OF D STAGE pH ON EFFLUENT QUALITY: CHARACTERIZATION OF EFFLUENT FRACTIONS FROM OD(EO) BLEACHING OF SOFTWOOD KRAFT PULP (1994 CPPA ANNUAL MEETING VERSION)

A condensed version of this paper appears in Section 4. This more complete version is included because it contains data for all effluent fractions.

THE EFFECT OF D STAGE PH ON EFFLUENT QUALITY: CHARACTERIZATION OF EFFLUENT FRACTIONS FROM OD(EO) BLEACHING OF SOFTWOOD KRAFT PULP

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ABSTRACT

Effluents from OD(EO) laboratory bleaching of softwood kraft pulp were characterized by fractionation and analysis of the fractions. The fractionation consisted of ether extraction followed by separation of the extract into acidic, phenolic, and neutral subfractions. The effluents from the sequence with the D stage begun at pH 2 (D-2 bleaching) were compared to the same sequence with the D stage begun at pH 4 (D-4 bleaching). Adsorbable organic halide (AOX) and total organic carbon (TOC) were determined for the whole D and (EO) effluents as well as for the fractions from both stages. Each fraction was characterized in terms of its ratio of chlorine to carbon (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}) and in terms of the proportion of total TOC within each fraction. The Cl/C_{100} is a likely predictor of environmental effects caused by certain effluent fractions.

The D-4 bleaching resulted in a reduced kappa number in the extracted pulp compared to the D-2 case. This is consistent with the whole effluent TOC data, in which D-4 bleaching produced more D stage TOC than the D-2. The (EO) stage TOC remained constant. The chlorine-to-carbon ratio decreased for each effluent type when D-4 bleaching was done.

The ether extractable material and the phenolic fraction, which both contain compounds of environmental interest, exhibited reduced Cl/C_{100} values when D-4 bleaching was done. Since the percentage of total TOC within these fractions increased, overall AOX levels were nearly constant, however. Because of the greater delignification at D-4 conditions, environmental and economic benefits may be realized by a reduction of the applied ClO_2 charge.

INTRODUCTION

It is generally accepted that bleaching at a pH of 2 or less results in greater delignification effectiveness for chlorine bleaching (1), for mixtures of chlorine and chlorine dioxide (2), and for chlorine dioxide alone (2, 3, 4, 5). However, an initial pH above 2 may be more effective in some cases (2, 3, 6).

The pH of a chlorination stage also has an effect on the quality of the effluent produced in the stage. The rates of formation of both chlorinated dioxins (7, 8) and chlorinated phenolic compounds (9, 10) are reduced by increased C stage pH. Total AOX is reduced at increased pH for both chlorine and chlorine dioxide bleaching (2).

Pulp bleaching effluents in general have been characterized with respect to adsorbable organic halide (AOX) (11-15) and in terms of individual compounds or environmentally significant groups of compounds such as chlorophenolics (9, 10, 15-21), chlorinated dioxins (7, 8, 18), chlorinated neutral compounds (21-23), chlorinated carboxylic acids (21, 24), and chloroform (17, 25).

Because of the complexity of pulp bleaching effluents, these analyses give an incomplete picture of their likely environmental effects. An alternative is summative analysis of the effluent by fractionation into meaningful classes of compounds, followed by relevant characterization of the fractions. One such procedure, based on ether extraction, has been developed and applied to effluents produced by D(EO), OD(EO), and OC(EO) sequences (26). Ether extraction was chosen as the basis for this procedure because virtually all effluent components known to be significant from an environmental standpoint are found in the extracts. Chlorine-to-carbon ratios (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}), which may predict environmental behavior, were determined for the fractions. The same fractionation and characterization methods were used for the present study of the effects of D stage initial pH in OD(EO) bleaching of softwood kraft pulp.

EXPERIMENTAL APPROACH

Pulp Bleaching

A mill-produced, oxygen-bleached kraft pulp with a kappa number of 14.1 was bleached by an OD(EO) sequence in the laboratory. Only the first two stages of bleaching were done, since most of the delignification and most of the effluent load production occurs in these stages. The D stages were done in a specially designed batch reactor, and the (EO) stages were done in a high shear mixer. The pH of the pulp slurry was adjusted to an initial level of 2 or 4 by the addition of sulfuric acid solution. Kappa numbers after bleaching are given in Table I.

Effluent Fractionation and Characterization

The effluents produced in this study were fractionated by ether extraction, and the ether extractable material was further separated into acidic, phenolic, and neutral fractions. To measure Cl/C_{100} on the ether extract and its fractions, the ether was exhaustively removed by evaporation, and AOX and TOC were then measured on each fraction. During evaporation, volatiles other than ether were also removed. To obtain information on the volatile fraction, a sample of the whole effluent was similarly evaporated and the carbon and chlorine losses determined.

Figure 1 depicts the effluent fractionation scheme, and Table II lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions: a non-extractable fraction and two ether extractable fractions. The first ether fraction is material readily extracted, and the second is removed slowly over an extended period. The first was further fractionated into acids, phenolics, and neutrals. Each fraction was then evaporated, as represented in Figure 1 by the dashed horizontal lines, to yield the final samples.

Data Analysis

The D-2 and D-4 bleaching sequences were performed in duplicate, and the effluents from the D and (EO) stages of bleaching were fractionated and analyzed separately. This resulted in two completely independent sets of data for each sequence. The data for all fractions are given in Tables III-X. The total TOC and AOX (given in Table III) represent TOC and AOX mass balances around the fractionation scheme, and were determined as the sums of the AOX and TOC measurements for the neutral, phenolic, acidic, polar, hydrophilic, and volatile fractions.

The data for individual fractions were interpreted principally in terms of their Cl/C_{100} values and their relative sizes, expressed as a percentage of total TOC. The Cl/C_{100} is of interest as a likely predictor of lipophilicity and toxicity within certain fractions.

Analyses of variance (AOV) were done on the data from each fraction to assess the significance of differences between pH levels and between stages. Since data with high Cl/C_{100} had a greater variance than the low Cl/C_{100} data, all Cl/C_{100} data were log transformed to stabilize variance. When AOV showed a significant effect between pH levels, a least significant difference was determined using Duncan's multiple range test (27).

RESULTS AND DISCUSSION

Whole Effluents

Data for the whole effluents are presented in Table III. The whole effluents contain 3.8-7.0 kg/t TOC and 0.1-0.4 kg/t AOX, depending on the stage and initial D stage pH.

Figure 2 compares mean effluent TOC from OD(EO) bleaching with the D stage begun at pH 4 (D-4 bleaching) and from the same sequence with the D stage begun at pH 2 (D-2 bleaching). In the D stage, and overall, the D-4 case results in the production of more effluent TOC. There is no increased TOC production in the (EO) stage following D-4 bleaching. A reduced kappa number is observed for the pulp from D-4 bleaching and could correspond to the higher level of TOC in the D stage effluent. The delignification of the pulp is discussed later in more detail.

Figure 3 presents a comparison of mean Cl/C_{100} for the whole effluents. Both the D and (EO) stage effluents individually have a greater Cl/C_{100} when D-2 bleaching is done. No overall difference is seen, however.

Ether Soluble Fraction

Table IV presents detailed data for the ether soluble fraction. This fraction contains 0.3-0.7 kg/t TOC, rep-

resenting 6-12% of the total TOC, and 0.01-0.08 kg/t AOX, representing 14-23% of the total AOX.

Figure 4 presents the mean ether soluble TOC as a percentage of total TOC for both pH levels. The mean TOC produced by D-4 bleaching is greater for each stage. Although the difference is not great enough to be statistically significant when all data are used, when the calculated value (see Table IV) is not included in the analysis, the difference is significant. This calculated value was eliminated from analysis because it is likely to contain greater error than measured values. It was determined from several measured values, each with individual errors.

Figure 5 similarly compares both pH levels with respect to Cl/C_{100}. The ether soluble fraction is chlorinated to a larger extent in both the D and (EO) stages when D-2 bleaching is done.

The reduced level of substitution by chlorine on organic material could be the result of a shift in chlorine containing species at pH 4 versus pH 2. Kolar and coworkers (28) reported that the sum of Cl_2 and HOCl during ClO_2 bleaching at pH 4.5 was reduced compared with similar bleaching at pH 2.5. Since Cl_2 and HOCl are responsible for chlorine substitution reactions (29, 30), an overall reduction in the level of these species would result in less substitution by chlorine atoms on organics in the effluent.

In addition to a reduction in the sum of Cl_2 and HOCl concentrations, a change in their ratio will occur. The Cl_2/HOCl equilibrium is such that HOCl is more favored as pH increases.

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

As acidity decreases, the equilibrium shifts to the right and to HOCl. Therefore, at pH 4 a greater proportion of the total chlorine exists as HOCl than at pH 2. Since HOCl is a less reactive chlorinating species (31), a reduced degree of chlorine substitution is expected at pH 4.

It is reasonable that a change in substitution behavior with pH will be more clearly seen in the ether soluble fractions. Chlorine substitutes to a greater extent on ether extractable material than on whole effluents (26). Therefore, these fractions are probably more sensitive to changes in substitution behavior than the whole effluents.

Since there is more ether soluble material formed by D-4 bleaching and that material is chlorinated to a reduced extent, the overall AOX remains essentially constant under both sets of conditions. This trend is repeated in other ether extractable fractions as well. This is consistent with the decreased tendency of ClO_2 to be involved in substitution of chlorine atoms at pH 4 and with the increased lignin fragmentation seen at pH 4, as indicated by the reduced kappa number achieved at constant chemical charge. Increased lignin fragmentation could be responsible for a greater proportion of material in the ether soluble fractions.

Phenolic Fraction

Detailed results of the analysis of the phenolic fraction are shown in Table V. The phenolic fraction contains 0.02-0.05 kg/t TOC or 0.5-0.7% of the total TOC, and 0.002-0.003 kg/t AOX or 0.8-2.6% of the total AOX.

Figure 6 compares the phenolic TOC as a percentage of total TOC for the two pH levels. In both the D and (EO) effluents, the phenolic fraction represents a higher percentage of the total TOC when the D stage is conducted at pH 4. Figure 7 shows the effect of pH on Cl/C_{100}. A decreased phenolic Cl/C_{100} is seen in the D-4 case.

Other Fractions

Data from the other effluent fractions displayed no statistically significant pH effects. This was generally due to small differences in means and scatter in the replicate data. Data and graphs for these fractions are provided so that the characterization is complete, and so that trends in the data may be observed. Replicate data for the neutral, acid, polar, hydrophilic, and the volatile fractions are provided in Tables VI-X. The corresponding graphs of the mean data are given in Figures 8-17.

It is interesting to note, that despite the lack of statistical significance, the other ether soluble fractions often maintain the trend observed with the ether soluble and phenolic fractions. On the average, the neutral, acid, and polar fractions all appear to contain a larger proportion of the total TOC when bleaching is conducted at pH 4, while the overall mean Cl/C_{100} is lower under D-4 conditions for the acid and polar fractions. Since a larger percentage of the material is extracted from effluents produced with D-4 bleaching, it is expected that the mean proportion of non-extractable

TOC should be lower under D-4 conditions (Figure 14), as is the case.

Degree of Delignification

The D stage effluent contains more TOC when the D stage is conducted at an initial pH of 4. The kappa number of the extracted pulp is reduced to 3.7 under D-4 conditions compared with 4.3 under D-2 conditions. The D+(EO) stage TOC, the kappa numbers, the change in pulp kappa number, and the ratio of TOC to kappa change are all given in Table I for the two pH levels. In an earlier study (26), it was stated that increased TOC per unit kappa loss may imply greater carbohydrate loss. Although the D stage begun at pH 4 appears to give slightly increased TOC per unit kappa loss, the apparent difference is not statistically significant.

In D-4 bleaching more delignification or kappa reduction can be done because less of the oxidizing power of ClO_2 may be wasted on other reaction types such as chlorine substitution reactions and chlorate (ClO_3^-) formation. A reaction byproduct of the oxidation of lignin by ClO_2 is chlorite ion (ClO_2^-) which may form chlorate or chlorine dioxide, depending on conditions, by the following reaction scheme (32, 33):

$$Cl_2 + ClO_2^- \longrightarrow Cl^- + [Cl_2O_2] \quad (1)$$

$$HOCl + ClO_2^- \longrightarrow OH^- + [Cl_2O_2] \quad (2)$$

$$[Cl_2O_2] \longrightarrow Cl^- + ClO_3^- \quad (3)$$

$$2[Cl_2O_2] \longrightarrow Cl_2 + 2ClO_2 \quad (4)$$

A high concentration of the reactive intermediate $[Cl_2O_2]$ favors the formation of ClO_2 by reaction 4 (second order in $[Cl_2O_2]$). Since chlorite ion is present in higher concentrations during pulp bleaching at pH 4 compared to pH 2 (28), reactions 1 and 2 (both first order in ClO_2^-) will produce increased levels of $[Cl_2O_2]$ at pH 4 and therefore more ClO_2 will be produced by reaction 4.

EXPERIMENTAL METHODS

Pulp Bleaching

A mill-produced, 14.1 kappa O_2-delignified southern softwood kraft pulp was used in this study. The pulp was collected just after the O_2 stage and was well washed before bleaching.

D Stages.

All D stages were done in a specially designed 20 L batch reactor. Bleaching was done at 2% consistency, at 45°C, for 30 minutes, and at a kappa factor of 0.25. The mixer was run at 350 rpm. Initial pH was adjusted to 2 or 4 by the addition of sulfuric acid solution.

(EO) Stages.

All (EO) stages were done in a Quantum Technologies high shear mixer at 10% consistency, at 70°C, and for 70 minutes. The NaOH charge was 0.55 times the total active chlorine charge; the O_2 charge was 0.5% on pulp; and 4.1% of the total D stage filtrate was included as carryover. The slurry was mixed at 15 hertz for 3 seconds, every 5 minutes.

Effluent Preparation

The D stage effluent was collected by filtration of the 2% slurry; the (EO) stage effluent was similarly collected after the 10% slurry was diluted to 2%. This was done to maintain a similar TOC content in all effluents for ether extraction. Effluent samples were filtered to remove any fibers, quenched with excess sodium sulfite, and acidified to a pH of less than 2. Ether extractions were always started within 2 days of effluent collection.

Ether Extraction of Effluents

Ether extraction was done on 4 L of effluent using continuous liquid-liquid extractors. Extraction was carried out with 500 ml of diethyl ether. The first ether phase was collected after 96 hours of extraction and was replaced with 500 ml of fresh ether. Extraction was continued for 336 total hours. The extraction was then stopped, and the second ether phase and the non-extractable materials were collected.

Ether Extract Fractionation

The first ether phase was diluted to 500 ml, 100 ml of the sample collected, and the remaining ether placed in a separatory funnel for fractionation. The ether was extracted 3 times with 25 ml of 0.5 M $NaHCO_3$, and the extracts were collected and acidified. The ether was next extracted 3 times with 25 ml of 0.5 M NaOH,

and these extracts were also collected and acidified. The $NaHCO_3$ soluble material is the acidic fraction; the NaOH soluble material is the phenolic fraction; and the remaining ether soluble material is the neutral fraction.

Sample Preparation

Ether was removed from all samples by evaporation to dryness, or near to dryness. The samples were then dissolved in water, acidified, and diluted to a known volume. To ensure reasonable sample recovery and to be certain the ether was removed, TOC and AOX mass balances were done around the fractionation scheme.

TOC Analysis

Measurement of TOC was done using a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate. Samples were prepared for TOC analysis by acidifying them, and sparging for 5 minutes with nitrogen to drive off any interfering carbonate species.

AOX Analysis

Measurement of AOX was done using a Dohrman model DX-20 organic halide analyzer. Sample preparation was done by a slight modification of method SCAN-W 9:89 (34). In this case samples were shaken for 4 hours rather 1 hour, to more completely adsorb the polar fractions.

SUMMARY AND CONCLUSIONS

An oxygen-bleached softwood kraft pulp was delignified to a greater extent by the OD(EO) sequence when the D stage was run at an initial pH of 4 compared to an initial pH of 2. D-4 bleaching resulted in a greater percentage of the total TOC within the environmentally significant ether soluble and phenolic fractions. However, the material within these fractions was substituted by chlorine atoms to a reduced extent under D-4 conditions. The net result was similar amounts of AOX at both pH levels.

Since D-4 bleaching causes increased D stage delignification, an equivalent amount of delignification can be done with less applied chemical, and an economic gain achieved. A reduced ClO_2 charge will result in less effluent AOX. Reducing the charge may also reduce the extent of lignin fragmentation and may reduce the proportion of material within the ether soluble fractions. If this proportion were reduced, the lower Cl/C_{100} values observed under D-4 conditions would represent a clear environmental advantage.

ACKNOWLEDGMENTS

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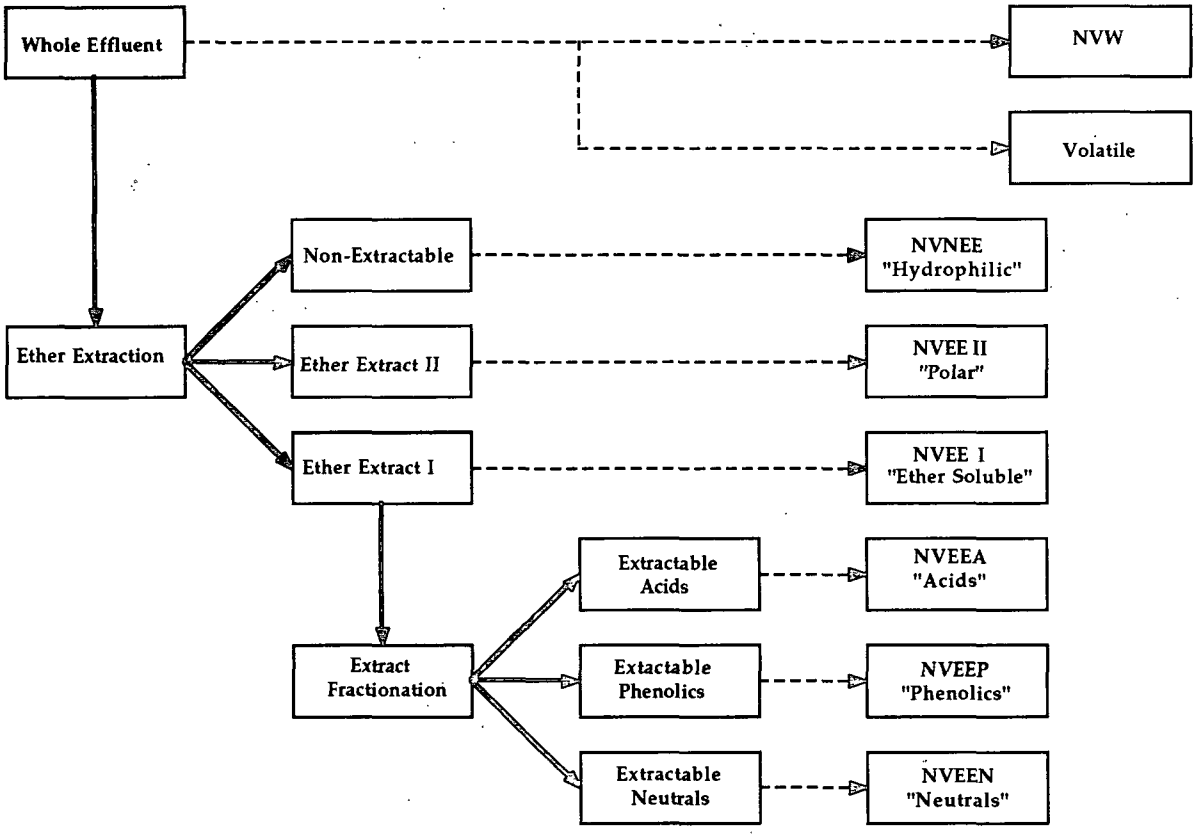
Figure 1. Effluent Fractionation.



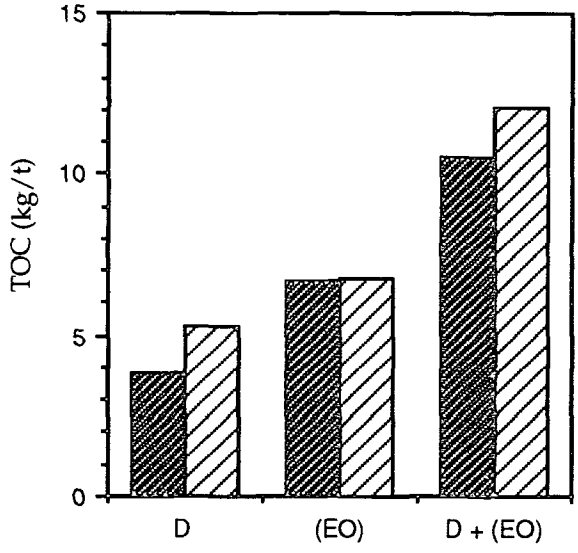


Figure 2. Whole effluent TOC.

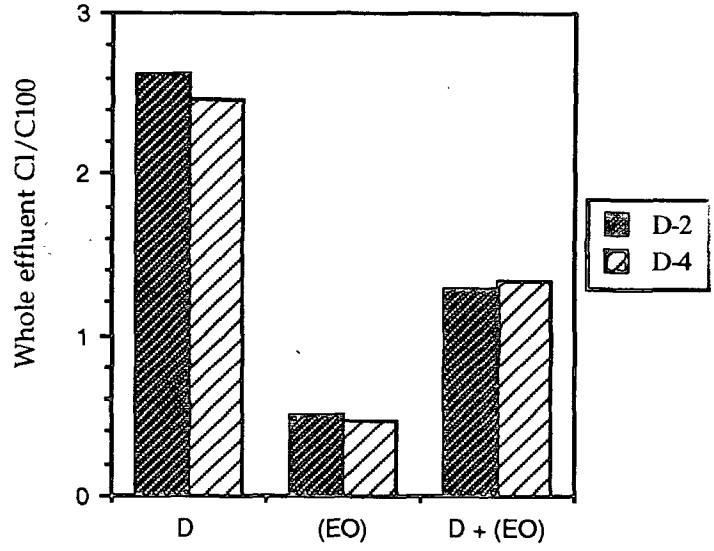


Figure 3. Whole effluent Cl/C100.

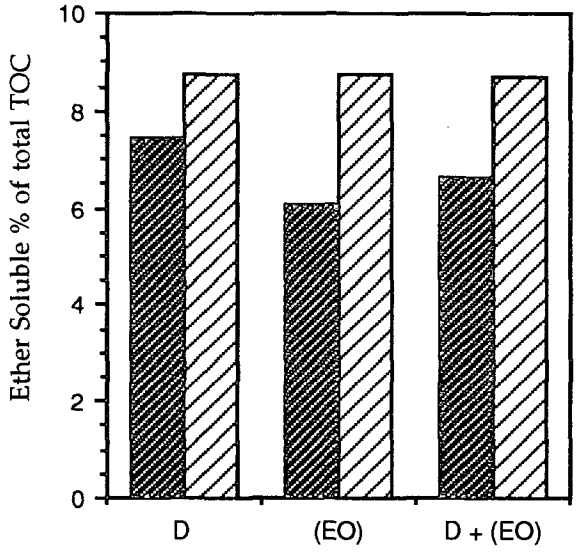


Figure 4. Ether Soluble % of total TOC.

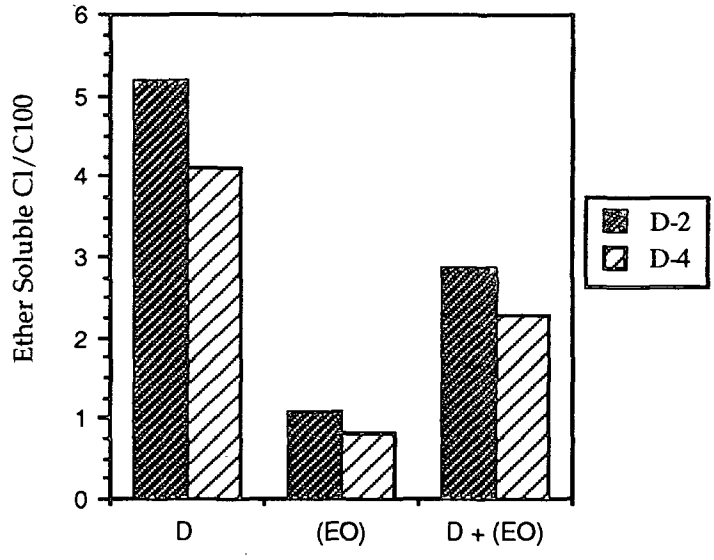


Figure 5. Ether Soluble Cl/C100.

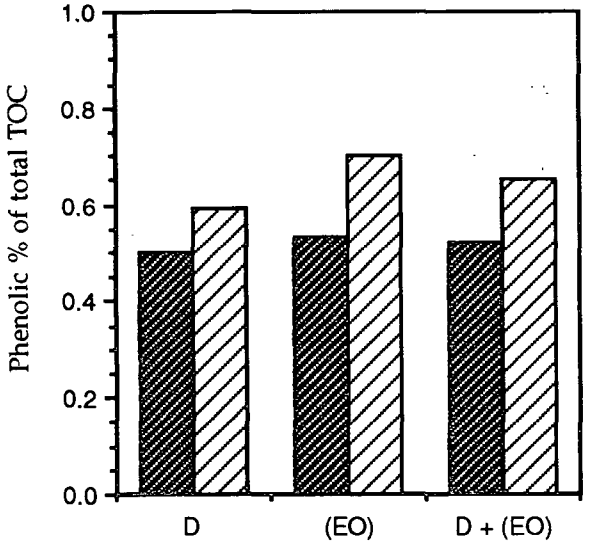


Figure 6. Phenolic % of total TOC.

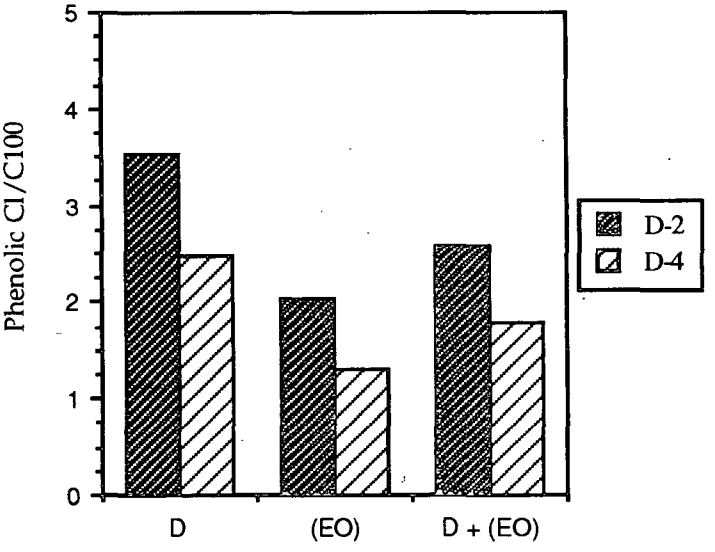


Figure 7. Phenolic Cl/C100.

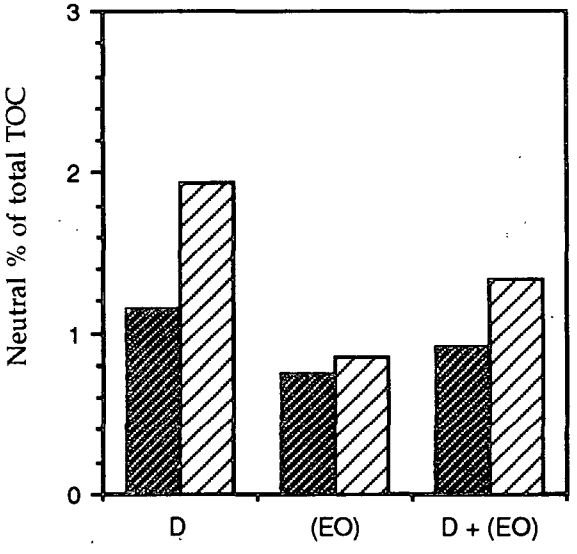


Figure 8. Neutral % of total TOC.

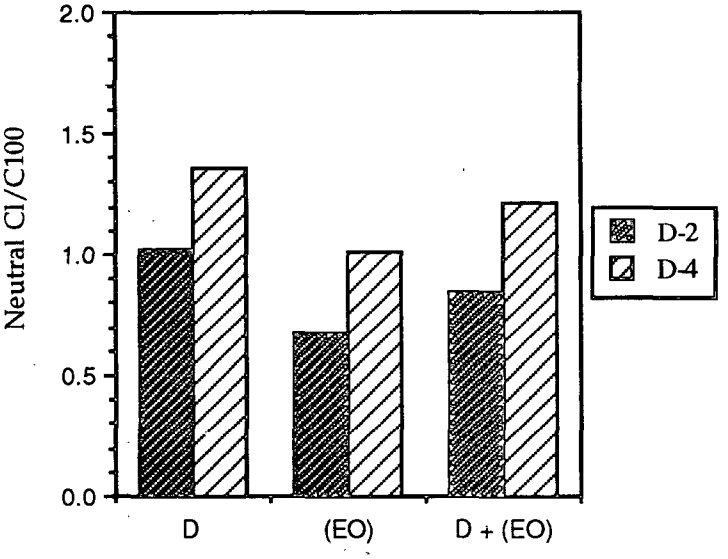


Figure 9. Neutral Cl/C100.

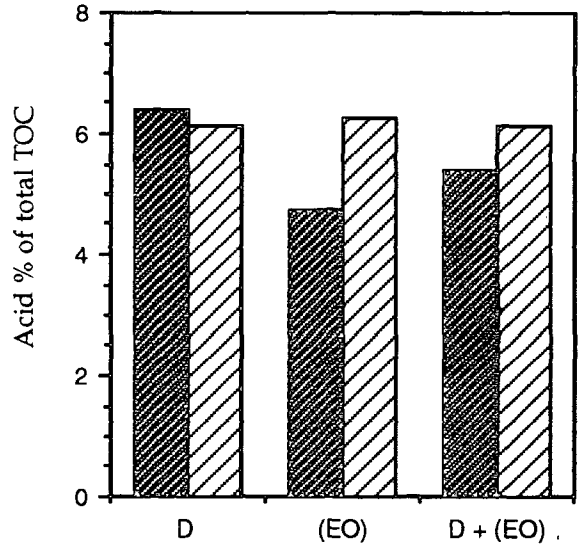


Figure 10. Acid % of total TOC.

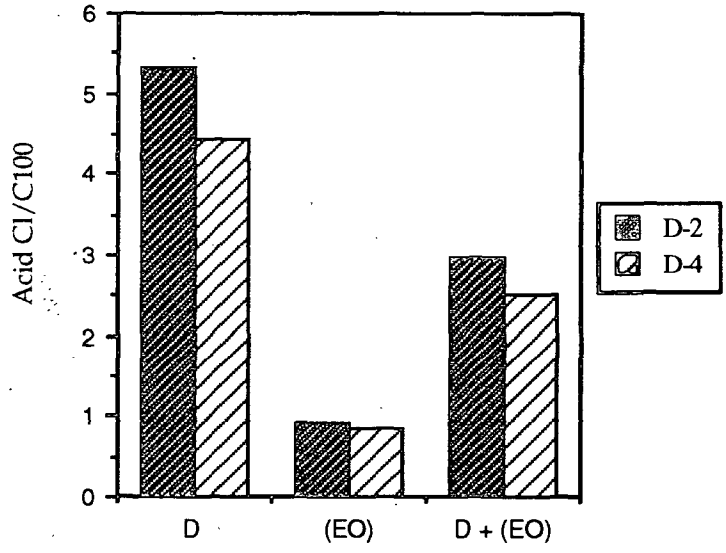


Figure 11. Acid Cl/C100.

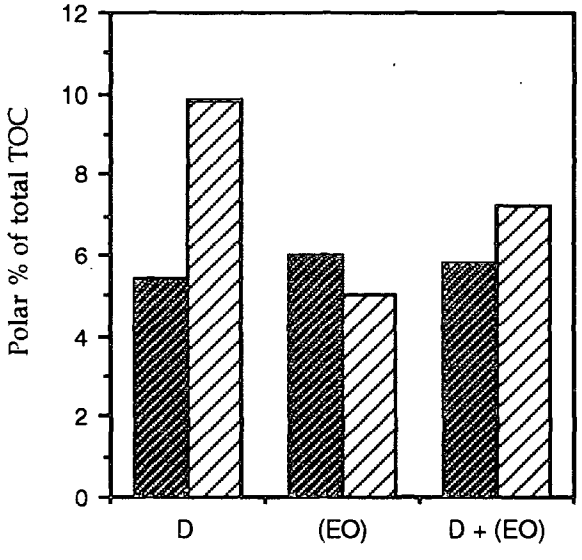


Figure 12. Polar % of total TOC.

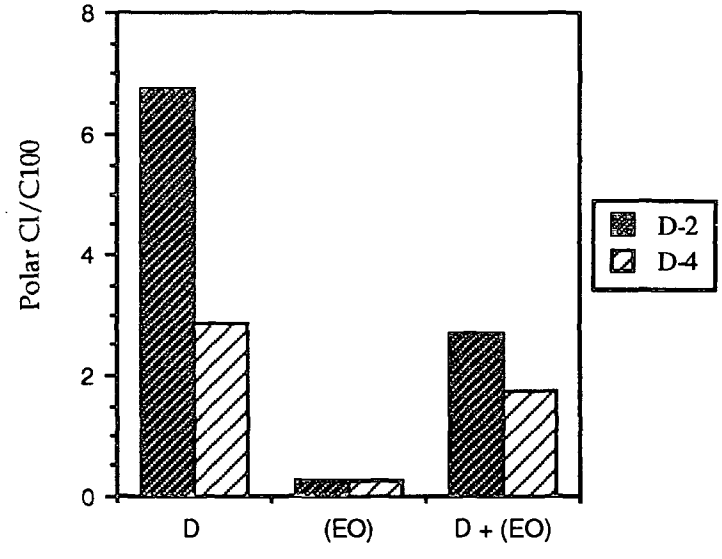


Figure 13. Polar Cl/C100.

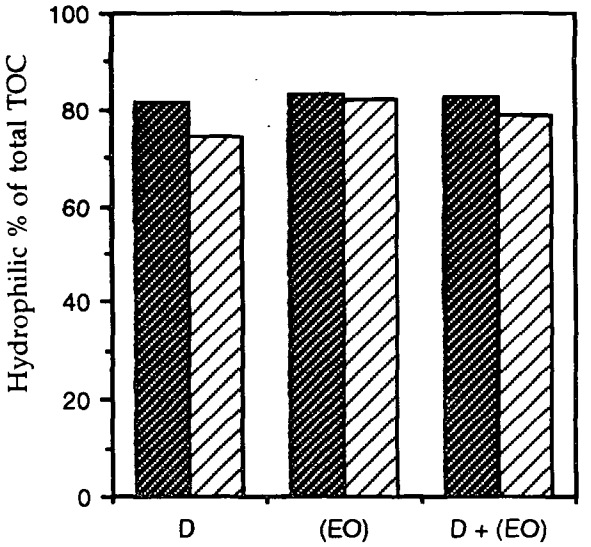


Figure 14. Hydrophilic % of total TOC.

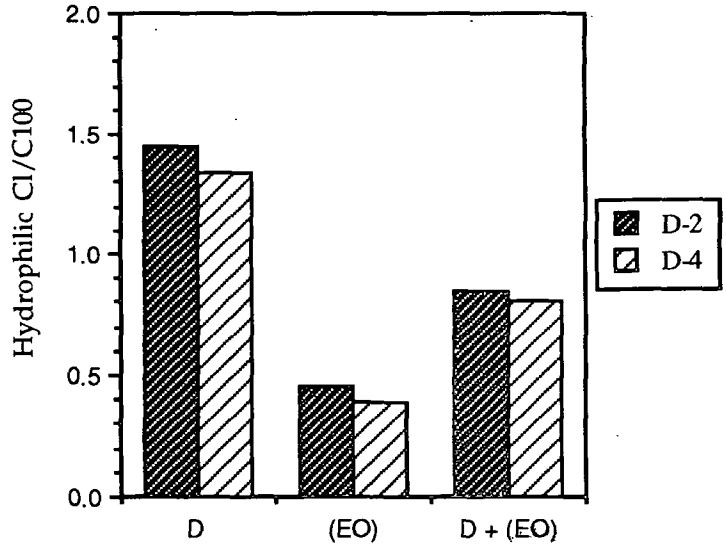


Figure 15. Hydrophilic Cl/C100.

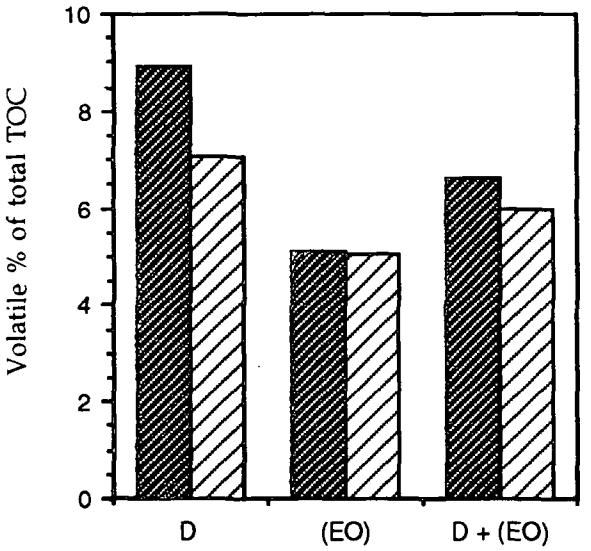


Figure 16. Volatile % of total TOC.

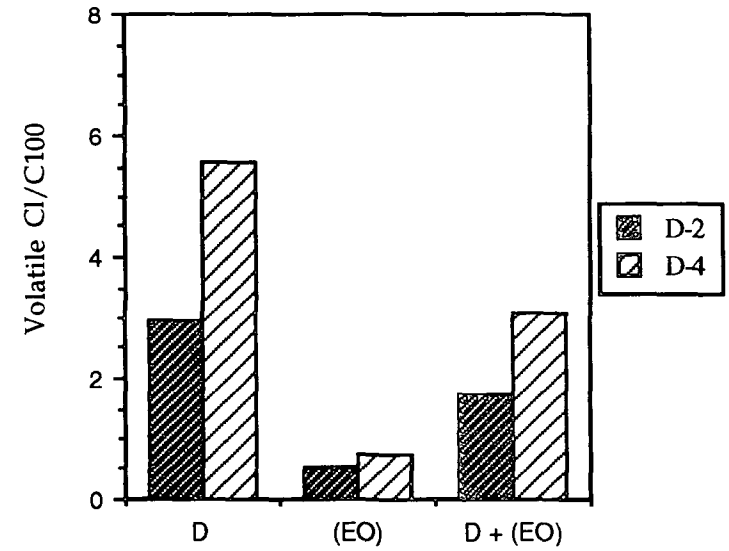


Figure 17. Volatile Cl/C100.

Table I. D+(EO) TOC and Kappa Number Data for OD(EO) Sequence.

D Stage Type	D + (EO) TOC (kg/t)	Kappa Number	Δ kappa	TOC/Δ kappa
D-2	10.6	4.23	9.87	1.07
D-2	10.4	4.44	9.66	1.08
D-4	12.4	3.70	10.40	1.19
D-4	11.7	3.71	10.39	1.13

Table II. Effluent Fraction Codes and Descriptions of Fractions.

Fraction Code	Description
NVW	Non-volatile, whole.
NVNEE	Non-volatile, non-ether extractable ("Hydrophilic").
NVEE II	Non-volatile, difficult to extract with ether ("Polar").
NVEE I	Non-volatile, readily ether extractable ("Ether Soluble").
NVEEA	Non-volatile, ether extractable acidic compounds ("Acids").
NVEEP	Non-volatile, ether extractable phenolic compounds ("Phenolics").
NVEEN	Non-volatile, ether extractable neutral compounds ("Neutrals").

Table III. Whole Effluent and Summed Fraction Characteristics.

D Stage	D-2		D-4	
TOC, kg/t	3.85	3.80	5.37	5.17
Total TOC[a], kg/t	4.43	4.29	5.55	6.64
AOX, kg/t	0.299	0.294	0.381	0.386
Total AOX[a], kg/t	0.297	0.264	0.337	0.336
Cl/C_{100}	2.63	2.61	2.40	2.53
(EO) Stage				
TOC, kg/t	6.79	6.60	7.01	6.54
Total TOC[a], kg/t	6.70	6.52	6.99	7.60
AOX, kg/t	0.101	0.102	0.0943	0.0929
Total AOX[a], kg/t	0.0938	0.0930	0.0983	0.0877
Cl/C_{100}	0.50	0.52	0.45	0.48
D Stage + (EO) Stage				
TOC, kg/t	10.6	10.4	12.38	11.71
Total TOC[a], kg/t	11.1	10.8	12.54	14.24
AOX, kg/t	0.400	0.396	0.475	0.479
Total AOX[a], kg/t	0.391	0.357	0.435	0.424
Cl/C_{100}	1.27	1.29	1.30	1.38

[a]Sum of corresponding values for volatile, hydrophilic, polar, acid, phenolic, and neutral fractions.

Table IV. Ether Soluble Fraction.

D Stage	D-2		D-4	
TOC, kg/t	0.383	0.267	0.643	0.388[a]
% of total TOC	8.65	6.22	11.6	5.85[a]
AOX, kg/t	0.0547	0.0439	0.0773	0.0474
% of total AOX	18.4	16.6	22.9	14.1
Cl/C_{100}	4.83	5.56	4.07	4.13[a]
(EO) Stage				
TOC, kg/t	0.406	0.399	0.532	0.748
% of total TOC	6.06	6.12	7.61	9.84
AOX, kg/t	0.0127	0.0125	0.0150	0.0154
% of total AOX	13.5	13.4	15.3	17.6
Cl/C_{100}	1.06	1.06	0.95	0.69
D Stage + (EO) Stage				
TOC, kg/t	0.789	0.666	1.175	1.136[a]
% of total TOC	7.09	6.16	9.37	7.98[a]
AOX, kg/t	0.0674	0.0564	0.0923	0.0628
% of total AOX	17.2	15.8	21.2	14.8
Cl/C_{100}	2.89	2.86	2.66	1.87[a]

[a]Determined from TOC balances. Sample was contaminated during evaporation.

Table V. Phenolic Fraction.

D Stage	**D-2**		**D-4**	
TOC, kg/t	0.0239	0.0198	0.0325	0.0389
% of total TOC	0.54	0.46	0.59	0.59
AOX, kg/t	0.00255	0.00201	0.00273	0.00239
% of total AOX	0.86	0.76	0.81	0.71
Cl/C_{100}	3.60	3.45	2.84	2.07
(EO) Stage				
TOC, kg/t	0.0364	0.0341	0.0513	0.0502
% of total TOC	0.54	0.52	0.73	0.66
AOX, kg/t	0.00243	0.00180	0.00216	0.00177
% of total AOX	2.59	1.94	2.20	2.02
Cl/C_{100}	2.26	1.79	1.42	1.19
D Stage + (EO) Stage				
TOC, kg/t	0.0603	0.0539	0.0838	0.0891
% of total TOC	0.54	0.50	0.67	0.63
AOX, kg/t	0.00498	0.00381	0.00489	0.00416
% of total AOX	1.27	1.07	1.12	0.98
Cl/C_{100}	2.79	2.39	1.97	1.58

Table VI. Neutral Fraction.

D Stage	**D-2**		**D-4**	
TOC, kg/t	0.0551	0.0457	0.175	0.0483
% of total TOC	1.24	1.07	3.15	0.73
AOX, kg/t	0.00153	0.00148	0.00350	0.00290
% of total AOX	0.52	0.56	1.04	0.86
Cl/C_{100}	0.94	1.09	0.68	2.03
(EO) Stage				
TOC, kg/t	0.0511	0.0480	0.0885	0.0313
% of total TOC	0.76	0.74	1.27	0.41
AOX, kg/t	0.00129	0.000701	0.00202	0.00114
% of total AOX	1.38	0.75	2.05	1.30
Cl/C_{100}	0.85	0.49	0.78	1.23
D Stage + (EO) Stage				
TOC, kg/t	0.106	0.0937	0.264	0.0796
% of total TOC	0.95	0.87	2.10	0.56
AOX, kg/t	0.00282	0.00218	0.00552	0.00404
% of total AOX	0.72	0.61	1.27	0.95
Cl/C_{100}	0.90	0.79	0.71	1.72

Table VII. Acid Fraction.

D Stage	D-2		D-4	
TOC, kg/t	0.316	0.242	0.428	0.301
% of total TOC	7.13	5.64	7.71	4.53
AOX, kg/t	0.0511	0.0369	0.0627	0.0350
% of total AOX	17.2	14.0	18.6	10.4
Cl/C_{100}	5.46	5.15	4.95	3.92
(EO) Stage				
TOC, kg/t	0.304	0.321	0.340	0.578
% of total TOC	4.54	4.92	4.86	7.61
AOX, kg/t	0.00856	0.00827	0.0105	0.0115
% of total AOX	9.13	8.89	10.7	13.1
Cl/C_{100}	0.95	0.87	1.04	0.67
D Stage + (EO) Stage				
TOC, kg/t	0.620	0.563	0.768	0.879
% of total TOC	5.57	5.21	6.12	6.17
AOX, kg/t	0.0597	0.0452	0.0732	0.0465
% of total AOX	15.3	12.7	16.8	11.0
Cl/C_{100}	3.25	2.71	3.22	1.79

Table VIII. Polar Fraction.

D Stage	D-2		D-4	
TOC, kg/t	0.226	0.248	0.386	0.848
% of total TOC	5.10	5.78	6.95	12.8
AOX, kg/t	0.0445	0.0502	0.0498	0.0336
% of total AOX	15.0	19.0	14.8	10.0
Cl/C_{100}	6.67	6.85	4.37	1.34
(EO) Stage				
TOC, kg/t	0.399	0.395	0.316	0.424
% of total TOC	5.96	6.06	4.52	5.58
AOX, kg/t	0.00333	0.00280	0.00269	0.00226
% of total AOX	3.55	3.01	2.74	2.58
Cl/C_{100}	0.28	0.24	0.29	0.18
D Stage + (EO) Stage				
TOC, kg/t	0.625	0.643	0.702	1.272
% of total TOC	5.62	5.95	5.60	8.93
AOX, kg/t	0.0478	0.0530	0.0525	0.0359
% of total AOX	12.2	14.8	12.1	8.46
Cl/C_{100}	2.59	2.79	2.53	0.95

Table IX. Hydrophilic Fraction.

D Stage	**D-2**		**D-4**	
TOC, kg/t	3.43	3.69	4.25	4.79
% of total TOC	77.4	86.0	76.6	72.1
AOX, kg/t	0.144	0.160	0.152	0.206
% of total AOX	48.5	60.6	45.1	61.3
Cl/C_{100}	1.42	1.47	1.21	1.46
(EO) Stage				
TOC, kg/t	5.50	5.45	5.84	6.13
% of total TOC	82.1	83.6	83.5	80.7
AOX, kg/t	0.0728	0.0745	0.0714	0.0644
% of total AOX	77.6	80.1	72.6	73.4
Cl/C_{100}	0.45	0.46	0.41	0.36
D Stage + (EO) Stage				
TOC, kg/t	8.93	9.14	10.09	10.92
% of total TOC	80.2	84.6	80.5	76.7
AOX, kg/t	0.217	0.235	0.223	0.270
% of total AOX	55.5	65.8	51.4	63.8
Cl/C_{100}	0.82	0.87	0.75	0.84

Table X. Volatile Fraction.

D Stage	D-2		D-4	
TOC, kg/t	0.380	0.396	0.276	0.609
% of total TOC	8.58	9.23	4.97	9.17
AOX, kg/t	0.0533	0.0136	0.0658	0.0557
% of total AOX	17.9	5.15	19.5	16.6
Cl/C_{100}	4.74	1.16	8.06	3.09
(EO) Stage				
TOC, kg/t	0.405	0.271	0.352	0.384
% of total TOC	6.04	4.16	5.04	5.05
AOX, kg/t	0.00539	0.00490	0.00956	0.00662
% of total AOX	5.75	5.27	9.73	7.55
Cl/C_{100}	0.45	0.61	0.92	0.58
D Stage + (EO) Stage				
TOC, kg/t	0.785	0.667	0.628	0.993
% of total TOC	7.05	6.17	5.01	6.97
AOX, kg/t	0.0587	0.0185	0.0754	0.0623
% of total AOX	15.0	5.18	17.3	14.7
Cl/C_{100}	2.53	0.94	4.06	2.12

APPENDIX 3: BLEACHING CONDITIONS

Oxidative Stage

Identification Code: DC4146-36
Date: 10-1-92
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.0
ClO_2 Concentration (g/L): 1.72
Total Oxidant Volume (L): 2.3
TAC (g): 10.40
TAC (% on pulp): 3.47
Kappa Factor (TAC, %/Kappa): 0.246
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 1.99
Final: 2.11
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 53.3
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 45.1
Measured: 47.2
Mixer Speed (rpm): 350
Reaction Time (sec.): 1800
Cl_2 Residual (g/L): 0.0533
Quenching Agent: n.a.
Quench Concentration (g/L): n.a.
Quench Volume (L): n.a.

Extraction Stage

Identification Code: $E_1$4146-36
Type: (EO) after DC4146-36
NaOH Concentration (g/L): 20
NaOH Volume (L): 0.290
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.91
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 600
Carryover (% of Oxidative Stage): 4.08
Total Stage Volume (L): 3.0
Dilution Water (L): 1.809
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): n.a.
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 2.0
Slurry pH (after dilution): 10.88
Extracted Kappa: 4.23

Oxidative Stage

Identification Code: DC4146-48
Date: 10-23-92
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.0
ClO_2 Concentration (g/L): 1.75
Total Oxidant Volume (L): 2.3
TAC (g): 10.59
TAC (% on pulp): 3.53
Kappa Factor (TAC, %/Kappa): 0.250
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 1.96
Final: 1.92
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): n.a.
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): n.a.
Measured: 47.3
Mixer Speed (rpm): 350
Reaction Time (sec.): 1800
Cl_2 Residual (g/L): 0.0780
Quenching Agent: n.a.
Quench Concentration (g/L): n.a.
Quench Volume (L): n.a.

Extraction Stage

Identification Code: $E_1$4146-49
Type: (EO) after DC4146-48
NaOH Concentration (g/L): 20
NaOH Volume (L): 0.290
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.94
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 600
Carryover (% of Oxidative Stage): 4.08
Total Stage Volume (L): 3.0
Dilution Water (L): 1.810
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): n.a.
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 2.0
Slurry pH (after dilution): 11.01
Extracted Kappa: 4.44

Oxidative Stage

Identification Code: DC4146-61
Date: 1-6-93
Type: 100% Cl_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 8.08
ClO_2 Concentration (g/L): 0.0
Total Oxidant Volume (L): 1.3
TAC (g): 10.50
TAC (% on pulp): 3.50
Kappa Factor (TAC, %/Kappa): 0.248
Pulp (g): 300
Water (g): 14,696
Consistency (%): 2.0
Slurry pH:
Initial: 2.01
Final: 1.78
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 50.0
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 45.6
Measured: n.a.
Mixer Speed (rpm): 350
Reaction Time (sec.): 1800
Cl_2 Residual (g/L): 0.0670
Quenching Agent: n.a.
Quench Concentration (g/L): n.a.
Quench Volume (L): n.a.

Extraction Stage

Identification Code: $E_1$4146-61
Type: (EO) after DC4146-61
NaOH Concentration (g/L): 20
NaOH Volume (L): 0.290
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.93
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 600
Carryover (% of Oxidative Stage): 4.08
Total Stage Volume (L): 3.0
Dilution Water (L): 1.809
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 10
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 2.0
Slurry pH (after dilution): 9.94
Extracted Kappa: 1.74

Oxidative Stage

Identification Code: DC4146-82
Date: 2-4-93
Type: 100% Cl_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 6.50
ClO_2 Concentration (g/L): 0.0
Total Oxidant Volume (L): 1.6
TAC (g): 10.40
TAC (% on pulp): 3.47
Kappa Factor (TAC, %/Kappa): 0.246
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 1.90
Final: 1.72
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 52.3
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 46.7
Measured: 49.0
Mixer Speed (rpm): 350
Reaction Time (sec.): 1800
Cl_2 Residual (g/L): 0.0426
Quenching Agent: n.a.
Quench Concentration (g/L): n.a.
Quench Volume (L): n.a.

Extraction Stage

Identification Code: $E_1$4146-82
Type: (EO) after DC4146-82
NaOH Concentration (g/L): 20
NaOH Volume (L): 0.318
NaOH Charge (% on pulp):
(0.60(TAC, % on pulp)): 2.08
NaOH Charge: (VC(100/P)): 2.12
Oxidative Stage Carryover (g): 600
Carryover (% of Oxidative Stage): 4.08
Total Stage Volume (L): 3.0
Dilution Water (L): 1.783
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 18
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 2.0
Slurry pH (after dilution): 10.35
Extracted Kappa: 2.10

Oxidative Stage

Identification Code: DC4146-94
Date: 3-2-93
Type: 100% ClO_2, Unbleached SW
Initial Kappa: 26.0
Cl_2 Concentration (g/L): 0.0
ClO_2 Concentration (g/L): 3.76
Total Oxidant Volume (L): 2.0
TAC (g): 19.80
TAC (% on pulp): 6.60
Kappa Factor (TAC, %/Kappa): 0.254
Pulp (g): 300
Water (g): 14,740
Consistency (%): 1.99
Slurry pH:
Initial: 1.98
Final: 1.84
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 50.4
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 43.7
Measured: 47.0
Mixer Speed (rpm): 350
Reaction Time (sec.): 1800
Cl_2 Residual (g/L): 0.0533
Quenching Agent: n.a.
Quench Concentration (g/L): n.a.
Quench Volume (L): n.a.

Extraction Stage

Identification Code: $E_1$4146-94
Type: (EO) after DC4146-94
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.272
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 3.63
NaOH Charge: (VC(100/P)): 3.63
Oxidative Stage Carryover (g): 600
Carryover (% of Oxidative Stage): 4.08
Total Stage Volume (L): 3.0
Dilution Water (L): 1.830
Consistency (%): 9.99
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 13
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 2.0
Slurry pH (after dilution): 10.50
Extracted Kappa: 5.27

Oxidative Stage

Identification Code: DC4146-113
Date: 4-15-93
Type: 100% ClO_2, Unbleached SW
Initial Kappa: 26.0
Cl_2 Concentration (g/L): 0.0
ClO_2 Concentration (g/L): 2.45
Total Oxidant Volume (L): 3.0
TAC (g): 19.32
TAC (% on pulp): 6.44
Kappa Factor (TAC, %/Kappa): 0.248
Pulp (g): 300
Water (g): 14,677
Consistency (%): 2.0
Slurry pH:
Initial: 1.94
Final: 1.91
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 53.8
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 43.0
Measured: 45.4
Mixer Speed (rpm): 350
Reaction Time (sec.): 1800
Cl_2 Residual (g/L): 0.0750
Quenching Agent: n.a.
Quench Concentration (g/L): n.a.
Quench Volume (L): n.a.

Extraction Stage

Identification Code: $E_1$4146-114
Type: (EO) after DC4146-113
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.270
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 3.58
NaOH Charge: (VC(100/P)): 3.60
Oxidative Stage Carryover (g): 600
Carryover (% of Oxidative Stage): 4.08
Total Stage Volume (L): 3.0
Dilution Water (L): 1.830
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 11
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 2.0
Slurry pH (after dilution): 10.95
Extracted Kappa: 4.83

Oxidative Stage

Identification Code: DC4146-125
Date: 5-1-93
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.0
ClO_2 Concentration (g/L): 3.059
Total Oxidant Volume (L): 1.3
TAC (g): 10.46
TAC (% on pulp): 3.49
Kappa Factor (TAC, %/Kappa): 0.247
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 4.08
Final: 2.51
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 53.0
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 48.4
Measured: 49.5
Mixer Speed (rpm): 350
Reaction Time (sec.): 1800
Cl_2 Residual (g/L): 0.0426
Quenching Agent: n.a.
Quench Concentration (g/L): n.a.
Quench Volume (L): n.a.

Extraction Stage

Identification Code: $E_1$4146-125
Type: (EO) after DC4146-125
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.145
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.94
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 600
Carryover (% of Oxidative Stage): 4.08
Total Stage Volume (L): 3.0
Dilution Water (L): 1.955
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 16
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 2.0
Slurry pH (after dilution): 10.64
Extracted Kappa: 3.70

Oxidative Stage

Identification Code: DC4146-136
Date: 5-15-93
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.0
ClO_2 Concentration (g/L): 3.145
Total Oxidant Volume (L): 1.3
TAC (g): 10.75
TAC (% on pulp): 3.58
Kappa Factor (TAC, %/Kappa): 0.254
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 3.83
Final: 2.45
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 50.0
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 45.7
Measured: 46.6
Mixer Speed (rpm): 350
Reaction Time (sec.): 1800
Cl_2 Residual (g/L): 0.0710
Quenching Agent: n.a.
Quench Concentration (g/L): n.a.
Quench Volume (L): n.a.

Extraction Stage

Identification Code: $E_1$4146-137
Type: (EO) after DC4146-136
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.145
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.97
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 600
Carryover (% of Oxidative Stage): 4.08
Total Stage Volume (L): 3.0
Dilution Water (L): 2.102
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 18
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 2.0
Slurry pH (after dilution): 10.80
Extracted Kappa: 3.71

Oxidative Stage

Identification Code: DC4146-149
Date: 5-31-93
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.0821
ClO_2 Concentration (g/L): 3.11
Total Oxidant Volume (L): 1.3
TAC (g): 10.73
TAC (% on pulp): 3.58
Kappa Factor (TAC, %/Kappa): 0.254
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 2.04
Final: 2.18
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 51.1
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 46.7
Measured: 45.1
Mixer Speed (rpm): 350
Reaction Time (sec.): 1800
Cl_2 Residual (g/L): n.a.
Quenching Agent: Na_2SO_3
Quench Concentration (g/L): 13
Quench Volume (L): 1.5

Extraction Stage

Identification Code: $E_1$4146-149
Type: (EO) after DC4146-149
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.145
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.97
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 0.0
Carryover (% of Oxidative Stage): 0.0
Total Stage Volume (L): 3.0
Dilution Water (L): 2.554
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 18
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 1.82
Slurry pH (after dilution): 10.85
Extracted Kappa: 4.37

Oxidative Stage

Identification Code: DC4146-174
Date: 6-27-93
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.0
ClO_2 Concentration (g/L): 3.13
Total Oxidant Volume (L): 1.3
TAC (g): 10.70
TAC (% on pulp): 3.57
Kappa Factor (TAC, %/Kappa): 0.253
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 2.14
Final: 2.14
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 51.0
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 46.6
Measured: 43.4
Mixer Speed (rpm): 350
Reaction Time (sec.): 60
Cl_2 Residual (g/L): n.a.
Quenching Agent: Na_2SO_3
Quench Concentration (g/L): 13
Quench Volume (L): 1.5

Extraction Stage

Identification Code: $E_1$4146-175
Type: (EO) after DC4146-174
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.145
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.96
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 0.0
Carryover (% of Oxidative Stage): 0.0
Total Stage Volume (L): 3.0
Dilution Water (L): 2.554
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 18
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 1.82
Slurry pH (after dilution): 10.78
Extracted Kappa: 5.89

Oxidative Stage

Identification Code: DC4207-25
Date: 9-11-93
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.0
ClO_2 Concentration (g/L): 3.14
Total Oxidant Volume (L): 1.3
TAC (g): 10.74
TAC (% on pulp): 3.58
Kappa Factor (TAC, %/Kappa): 0.254
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 2.08
Final: 2.28
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 50.2
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 45.8
Measured: 43.5
Mixer Speed (rpm): 350
Reaction Time (sec.): 3
Cl_2 Residual (g/L): n.a.
Quenching Agent: Na_2SO_3
Quench Concentration (g/L): 13
Quench Volume (L): 1.5

Extraction Stage

Identification Code: $E_1$4207-25
Type: (EO) after DC4207-25
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.145
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.97
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 0.0
Carryover (% of Oxidative Stage): 0.0
Total Stage Volume (L): 3.0
Dilution Water (L): 2.560
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 20
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 1.82
Slurry pH (after dilution): 11.02
Extracted Kappa: 8.23

Oxidative Stage

Identification Code: DC4207-34
Date: 10-3-93
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.0
ClO_2 Concentration (g/L): 3.10
Total Oxidant Volume (L): 1.3
TAC (g): 10.60
TAC (% on pulp): 3.53
Kappa Factor (TAC, %/Kappa): 0.250
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 2.08
Final: 2.29
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 49.2
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 44.9
Measured: 42.5
Mixer Speed (rpm): 350
Reaction Time (sec.): 300
Cl_2 Residual (g/L): n.a.
Quenching Agent: Na_2SO_3
Quench Concentration (g/L): 13
Quench Volume (L): 1.5

Extraction Stage

Identification Code: $E_1$4207-34
Type: (EO) after DC4207-34
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.145
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.94
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 0.0
Carryover (% of Oxidative Stage): 0.0
Total Stage Volume (L): 3.0
Dilution Water (L): 2.560
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 20
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 1.82
Slurry pH (after dilution): 11.30
Extracted Kappa: 5.17

Oxidative Stage

Identification Code: DC4207-51
Date: 10-17-93
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.009
ClO_2 Concentration (g/L): 3.16
Total Oxidant Volume (L): 1.3
TAC (g): 10.67
TAC (% on pulp): 3.56
Kappa Factor (TAC, %/Kappa): 0.253
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 2.11
Final: 2.18
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 50.5
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 46.1
Measured: n.a.
Mixer Speed (rpm): 350
Reaction Time (sec.): 60
Cl_2 Residual (g/L): n.a.
Quenching Agent: Na_2SO_3
Quench Concentration (g/L): 13
Quench Volume (L): 1.5

Extraction Stage

Identification Code: $E_1$4207-51
Type: (EO) after DC4207-51
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.145
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.96
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 0.0
Carryover (% of Oxidative Stage): 0.0
Total Stage Volume (L): 3.0
Dilution Water (L): 2.560
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 18
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 1.82
Slurry pH (after dilution): 11.43
Extracted Kappa: 6.56

Oxidative Stage

Identification Code: DC4207-68
Date: 11-13-93
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.0
ClO_2 Concentration (g/L): 3.15
Total Oxidant Volume (L): 1.3
TAC (g): 10.76
TAC (% on pulp): 3.59
Kappa Factor (TAC, %/Kappa): 0.254
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 2.11
Final: 2.30
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 50.5
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 46.1
Measured: 44.2
Mixer Speed (rpm): 350
Reaction Time (sec.): 300
Cl_2 Residual (g/L): n.a.
Quenching Agent: Na_2SO_3
Quench Concentration (g/L): 13
Quench Volume (L): 1.5

Extraction Stage

Identification Code: $E_1$4207-68
Type: (EO) after DC4207-68
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.145
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.97
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 0.0
Carryover (% of Oxidative Stage): 0.0
Total Stage Volume (L): 3.0
Dilution Water (L): 2.560
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 20
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 1.82
Slurry pH (after dilution): 10.94
Extracted Kappa: 5.79

Oxidative Stage

Identification Code: DC4207-81
Date: 12-12-93
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.0
ClO_2 Concentration (g/L): 3.11
Total Oxidant Volume (L): 1.3
TAC (g): 10.63
TAC (% on pulp): 3.54
Kappa Factor (TAC, %/Kappa): 0.251
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 2.25
Final: 2.52
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 51.2
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 46.8
Measured: 42.3
Mixer Speed (rpm): 350
Reaction Time (sec.): 3
Cl_2 Residual (g/L): n.a.
Quenching Agent: Na_2SO_3
Quench Concentration (g/L): 13
Quench Volume (L): 1.5

Extraction Stage

Identification Code: $E_1$4207-81
Type: (EO) after DC4207-81
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.145
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.95
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 0.0
Carryover (% of Oxidative Stage): 0.0
Total Stage Volume (L): 3.0
Dilution Water (L): 2.550
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 18
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 1.82
Slurry pH (after dilution): 11.31
Extracted Kappa: 7.11

Oxidative Stage

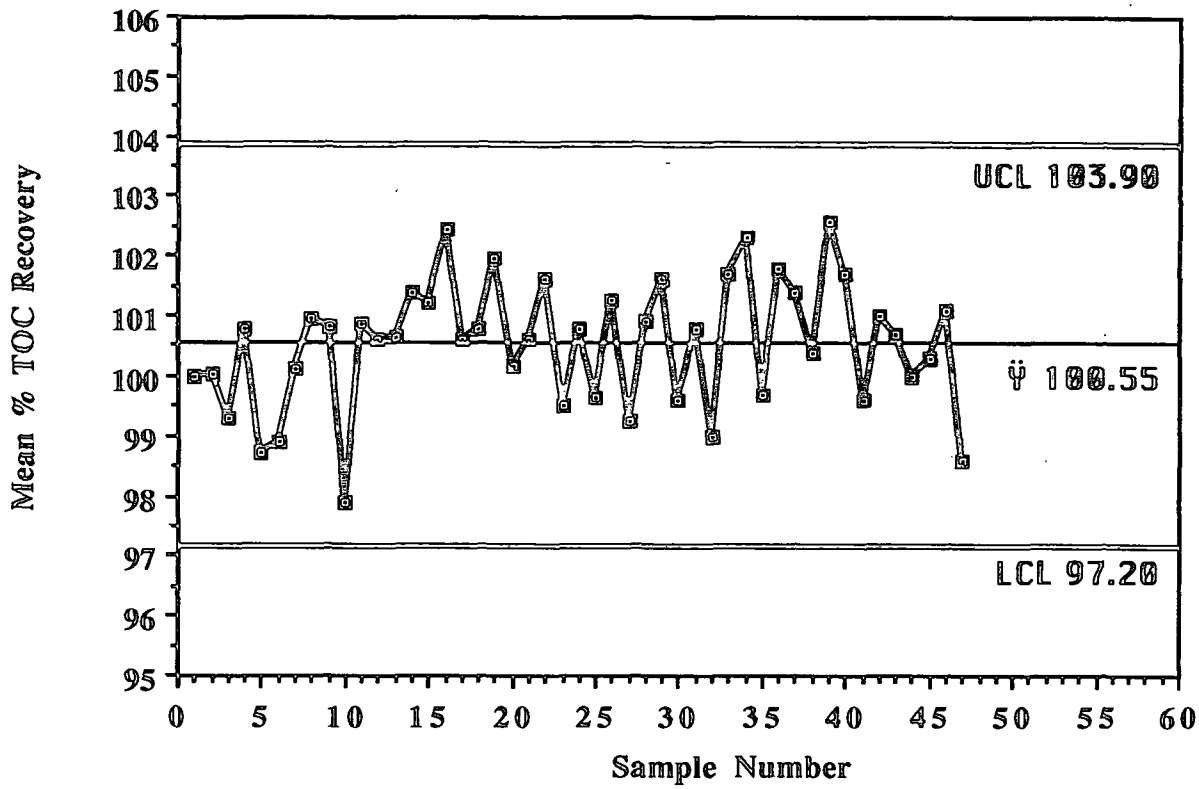
Identification Code: DC4207-95
Date: 1-8-94
Type: 100% ClO_2, O_2 bleached SW
Initial Kappa: 14.1
Cl_2 Concentration (g/L): 0.013
ClO_2 Concentration (g/L): 3.15
Total Oxidant Volume (L): 1.3
TAC (g): 10.78
TAC (% on pulp): 3.59
Kappa Factor (TAC, %/Kappa): 0.255
Pulp (g): 300
Water (g): 14,700
Consistency (%): 2.0
Slurry pH:
Initial: 1.85
Final: 2.03
Oxidant Temp. (°C): 0
Initial Slurry Temp. (°C): 51.7
Final Slurry Temp. (°C):
Calculated ($T_f=T_i/1+(W_c/W_h)$): 47.2
Measured: 45.3
Mixer Speed (rpm): 350
Reaction Time (sec.): 1800
Cl_2 Residual (g/L): n.a.
Quenching Agent: Na_2SO_3
Quench Concentration (g/L): 13
Quench Volume (L): 1.5

Extraction Stage

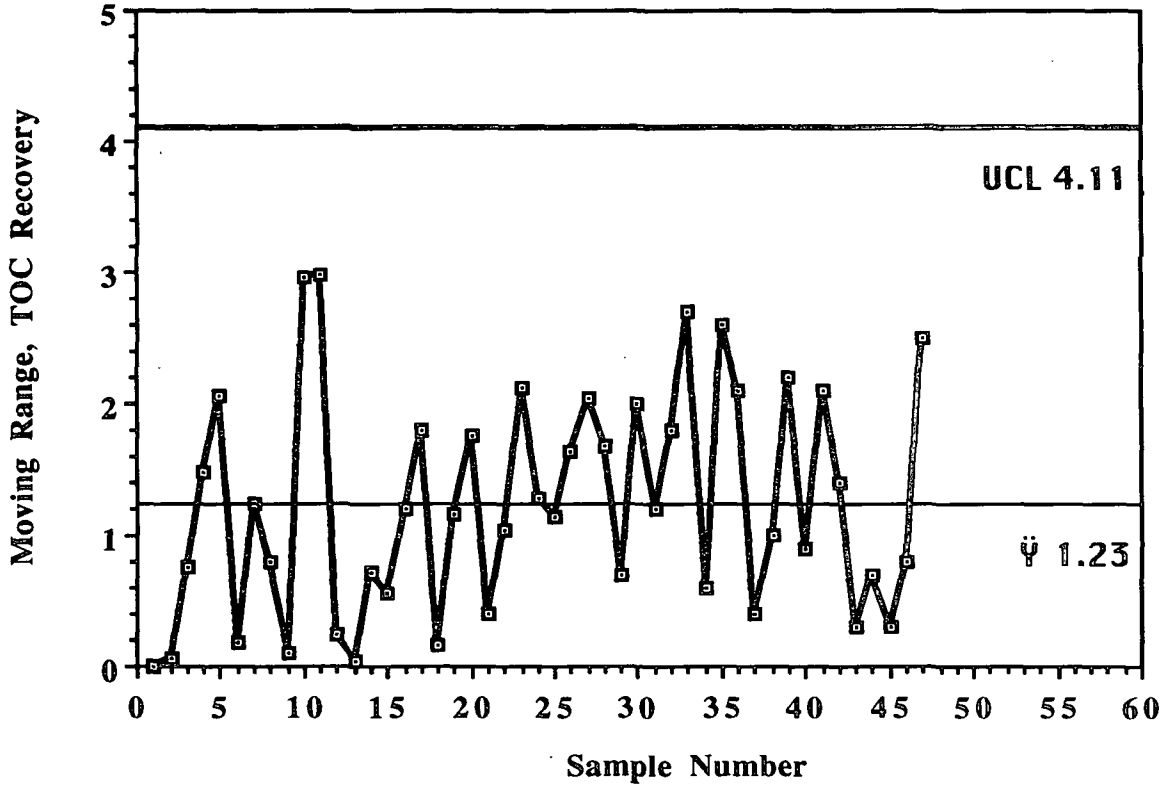
Identification Code: $E_1$4207-95
Type: (EO) after DC4207-95
NaOH Concentration (g/L): 40
NaOH Volume (L): 0.145
NaOH Charge (% on pulp):
(0.55(TAC, % on pulp)): 1.93
NaOH Charge: (VC(100/P)): 1.93
Oxidative Stage Carryover (g): 0.0
Carryover (% of Oxidative Stage): 0.0
Total Stage Volume (L): 3.0
Dilution Water (L): 2.560
Consistency (%): 10.0
Temperature (°C): 70
Reaction Time (min.): 70
Reactor Pressure (psig): 20
O_2 Volume (L): 1.1
O_2 Pressure (atm.): 1
O_2 Charge (% on pulp): PV(0.4365): 0.48
Slurry Consistency (after dilution): 1.82
Slurry pH (after dilution): 11.38
Extracted Kappa: 4.98

APPENDIX 4: TOC STANDARD CONTROL CHARTS

Appendix 4A: TOC Standard Recovery Mean Control Chart



Appendix 4B: TOC Standard Recovery Moving Range Control Chart

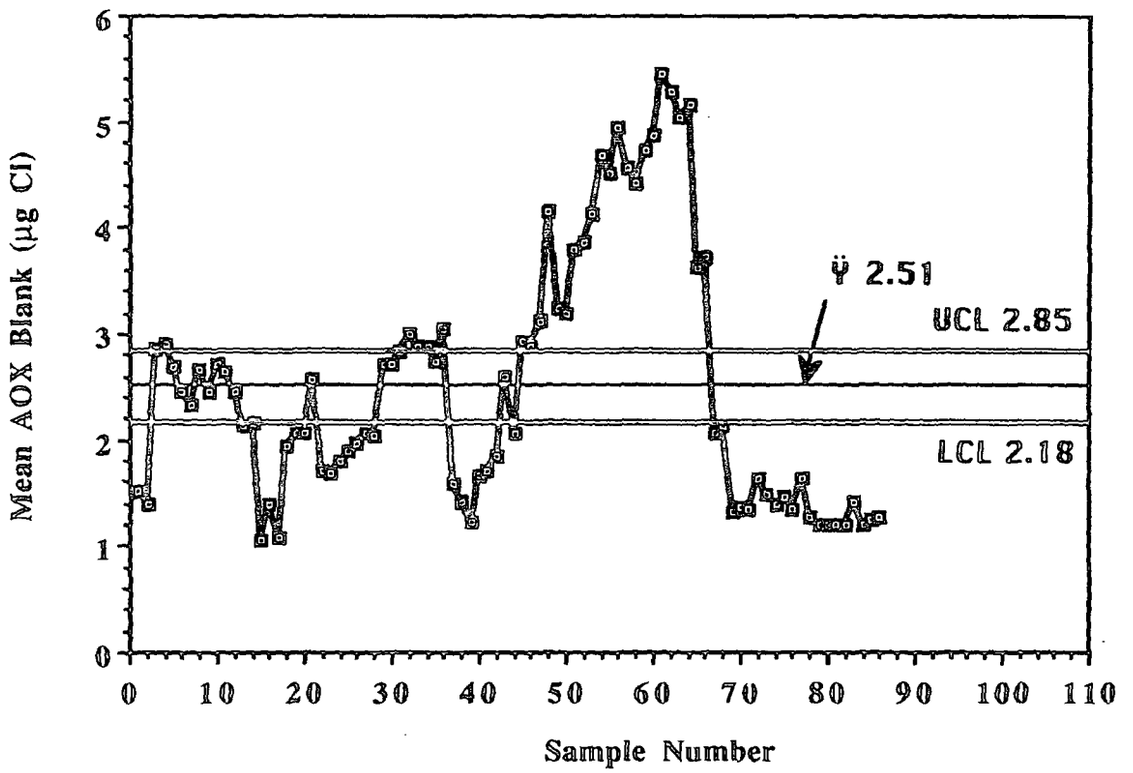


Appendix 4C: TOC Standard Recovery Control Chart Data

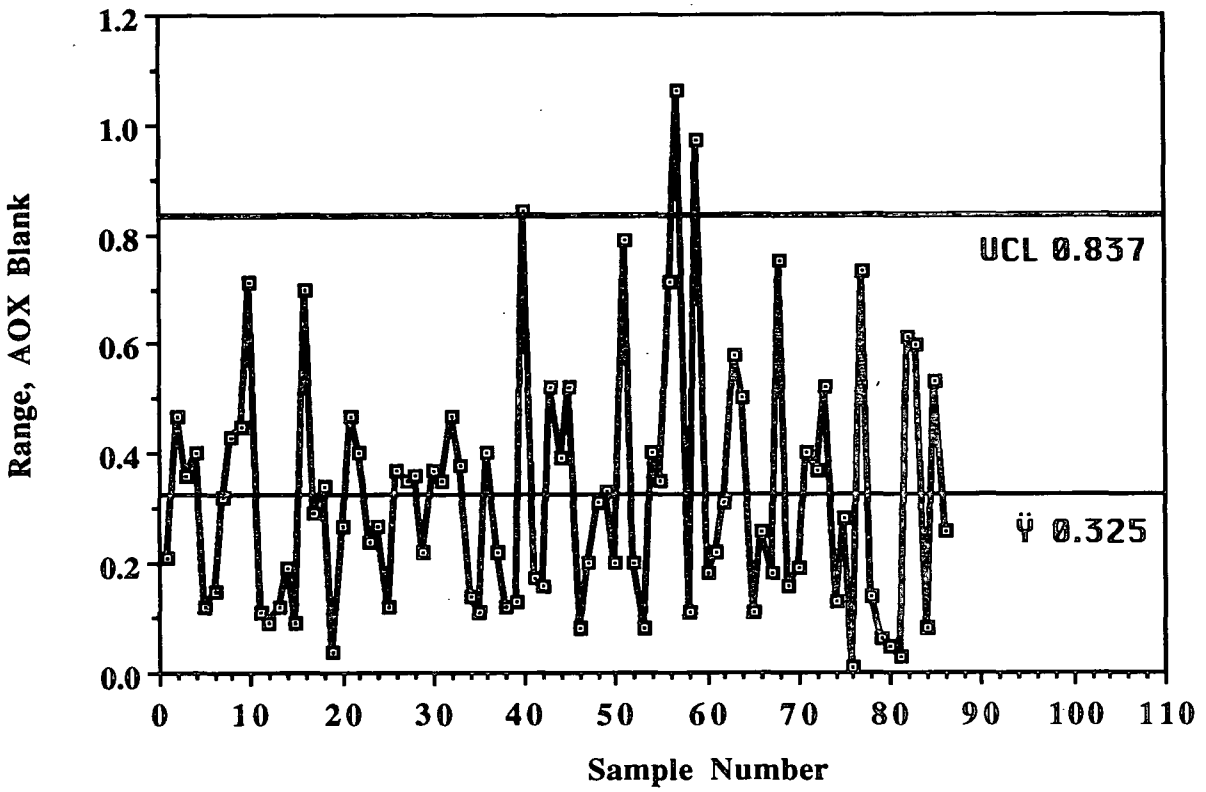
Number	Identification Code	Standard Recovery (%)	Moving Range
1	4059-16	100.0	----
2	4059-23	100.0	0.0
3	4059-28	99.3	0.7
4	4059-33	100.8	1.5
5	4059-40	98.7	2.1
6	4059-49	98.9	0.2
7	4059-57	100.1	1.2
8	4059-73	102.0	0.9
9	4059-82	100.9	0.1
10	4146-23	97.9	3.0
11	4146-27	100.9	3.0
12	4146-31	100.6	0.3
13	4146-43	100.7	0.1
14	4146-50	101.4	0.7
15	4146-54	101.2	0.2
16	4146-58	102.4	1.2
17	4146-69	100.6	1.8
18	4146-75	100.8	0.2
19	4146-79	102.0	1.2
20	4146-87	100.2	1.8
21	4146-89	100.6	0.4
22	4146-91	101.6	1.0
23	4146-98	99.5	2.1
24	4146-104	100.8	1.3
25	4146-120	99.6	1.2
26	4146-132	101.3	1.7
27	4146-142	99.2	2.1
28	4146-148	100.9	1.7
29	4146-152	101.6	0.7
30	4146-171	99.6	2.0
31	4146-185	100.8	1.2
32	4146-191	99.0	1.8
33	4207-4	101.7	2.7
34	4207-7	102.3	0.6
35	4207-13	99.7	2.6
36	4207-23	101.8	2.1
37	4207-28	101.4	0.4
38	4207-32	100.4	1.0
39	4207-39	102.6	2.2
40	4207-46	101.7	0.9
41	4207-57	99.6	2.1
42	4207-64	101.0	1.4
43	4207-67	100.7	0.3
44	4207-71	100.0	0.7
45	4207-77	100.3	0.3
46	4207-93	101.1	0.8
47	4207-108	98.6	2.5

APPENDIX 5: AOX BLANK CONTROL CHARTS

Appendix 5A: AOX Blank Mean Control Chart



Appendix 5B: AOX Blank Range Control Chart

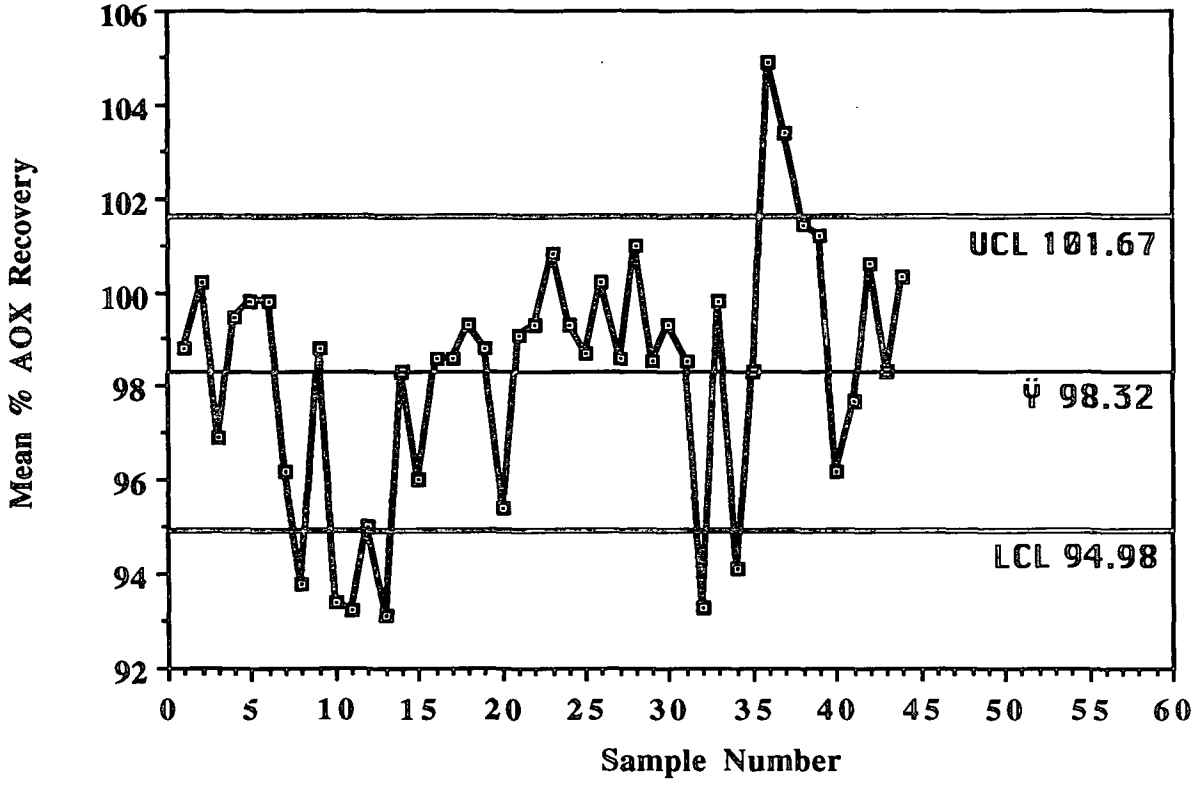


Appendix 5C: AOX Blank Control Chart Data

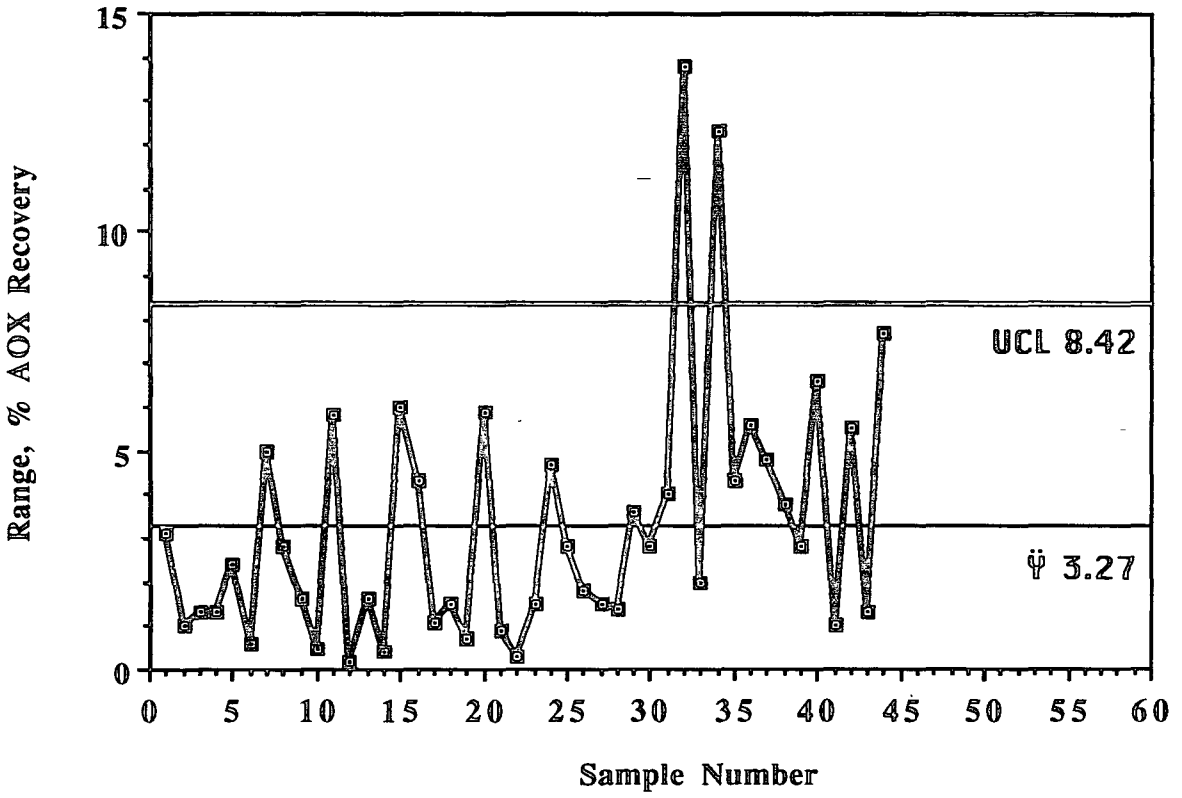
Number	Identification Code	Blank (µg Cl)	Range
1	4059-180-	1.52	0.21
2	4059-187	1.40	0.47
3	4146-25	2.85	0.36
4	4146-30	2.90	0.40
5	4146-33	2.69	0.12
6	4146-38	2.44	0.15
7	4146-41	2.32	0.32
8	4146-46	2.67	0.43
9	4146-53	2.45	0.45
10	4146-57	2.71	0.71
11	4146-60	2.63	0.11
12	4146-65	2.46	0.09
13	4146-68	2.13	0.12
14	4146-75	2.15	0.19
15	4146-80	1.06	0.09
16	4146-86	1.38	0.70
17	4146-90	1.07	0.29
18	4146-92	1.94	0.34
19	4146-102	2.06	0.04
20	4146-106	2.06	0.27
21	4146-112	2.56	0.47
22	4146-119	1.71	0.40
23	4146-124	1.69	0.24
24	4146-130	1.80	0.27
25	4146-134	1.89	0.12
26	4146-143	1.97	0.37
27	4146-147	2.06	0.35
28	4146-153	2.03	0.36
29	4146-158	2.70	0.22
30	4146-159	2.72	0.37
31	4146-167	2.84	0.35
32	4146-167	2.99	0.47
33	4146-170	2.88	0.38
34	4146-170	2.89	0.14
35	4146-178	2.74	0.11
36	4146-178	3.04	0.40
37	4146-184	1.59	0.22
38	4146-187	1.42	0.12
39	4207-3	1.23	0.13
40	4207-3	1.65	0.84
41	4207-6	1.71	0.17
42	4207-6	1.85	0.16
43	4207-12	2.60	0.52
44	4207-13	2.07	0.39
45	4207-17	2.93	0.52
46	4207-17	2.88	0.08
47	4207-23	3.12	0.20
48	4207-23	4.16	0.31
49	4207-31	3.25	0.33
50	4207-31	3.20	0.20

Number	Identification Code	Blank (µg Cl)	Range
51	4207-37	3.78	0.79
52	4207-37	3.87	0.20
53	4207-41	4.13	0.08
54	4207-41	4.68	0.40
55	4207-44	4.52	0.35
56	4207-44	4.95	0.71
57	4207-48	4.56	1.06
58	4207-48	4.41	0.11
59	4207-55	4.72	0.97
60	4207-55	4.86	0.18
61	4207-60	5.46	0.22
62	4207-60	5.28	0.31
63	4207-63	5.03	0.58
64	4207-63	5.17	0.50
65	4207-66	3.62	0.11
66	4207-66	3.72	0.26
67	4207-67	2.06	0.18
68	4207-67	2.13	0.75
69	4207-72	1.32	0.16
70	4207-72	1.36	0.19
71	4207-76	1.35	0.40
72	4207-77	1.62	0.37
73	4207-78	1.48	0.52
74	4207-78	1.40	0.13
75	4207-84	1.46	0.28
76	4207-84	1.35	0.01
77	4207-90	1.63	0.73
78	4207-90	1.26	0.14
79	4207-93	1.20	0.06
80	4207-93	1.21	0.05
81	4207-102	1.21	0.03
82	4207-102	1.20	0.61
83	4207-105	1.41	0.60
84	4207-105	1.21	0.08
85	4207-107	1.25	0.53
86	4207-107	1.27	0.26

Appendix 6A: AOX Standard Recovery Mean Control Chart



Appendix 6B: AOX Standard Recovery Range Control Chart



Appendix 6C: AOX Standard Recovery Control Chart Data

Number	Identification Code	Standard Recovery (%)	Range
1	4059-180	98.8	3.1
2	4146-24	100.2	1.0
3	4146-26	96.9	1.3
4	4146-30	99.5	1.3
5	4146-38	99.8	2.4
6	4146-41	99.8	0.6
7	4146-57	96.2	5.0
8	4146-65	93.8	2.8
9	4146-68	98.8	1.6
10	4146-80	93.4	0.5
11	4146-90	93.2	5.8
12	4146-106	95.0	0.2
13	4146-111	93.1	1.6
14	4146-119	98.3	0.4
15	4146-124	96.0	6.0
16	4146-130	98.6	4.3
17	4146-134	98.6	1.1
18	4146-143	99.3	1.5
19	4146-147	98.8	0.7
20	4146-153	95.4	5.9
21	4146-158	99.1	0.9
22	4146-158	99.3	0.3
23	4146-159	100.8	1.5
24	4146-167	99.3	4.7
25	4146-178	98.7	2.8
26	4146-184	100.2	1.8
27	4146-187	98.6	1.5
28	4207-3	101.0	1.4
29	4207-6	98.5	3.6
30	4207-13	99.3	2.8
31	4207-17	98.5	4.0
32	4207-23	93.3	13.8
33	4207-31	99.8	2.0
34	4207-37	94.1	12.3
35	4207-41	98.3	4.3
36	4207-44	104.9	5.6
37	4207-48	103.4	4.8
38	4207-55	101.4	3.8
39	4207-60	101.2	2.8
40	4207-63	96.2	6.6
41	4207-90	97.7	1.0
42	4207-102	100.6	5.5
43	4207-105	98.3	1.3
44	4207-107	100.3	7.7

APPENDIX 7: LOTUS SPREADSHEET FOR AOX AND TOC BALANCE CALCULATION AND CHLORINE TO CARBON RATIO DETERMINATION

Appendix 7A contains a printout of the Lotus 123 spreadsheet that was used to calculate AOX and TOC balances and to determine the chlorine to carbon ratio for each effluent fraction. This printout shows the formulas used in these calculations. Appendix 7B provides instructions for using the spreadsheet.

Appendix 7A: Lotus Spreadsheet

	A	B
1	Effluent Number	Effluent Fraction
2	_____	Whole
3		NVW
4		NVEE I
5		NVEE II
6		NVNEE
7		NVEEA
8		NVEEP
9		NVEEN
10		Volatiles
11		
12		
13		
14		
15		
16		
17		
18		
19		
20		
21		
22		
23		
24		
25		
26		
27		
28		
29		
30		

	C	D
1	% Fullscale *	TOC (dilution) *
2	_____	(D2=A+(B*C2)+(C*((C2)^2)))
3	_____	(D3=A+(B*C3)+(C*((C3)^2)))
4	_____	(D4=A+(B*C4)+(C*((C4)^2)))
5	_____	(D5=A+(B*C5)+(C*((C5)^2)))
6	_____	(D6=A+(B*C6)+(C*((C6)^2)))
7	_____	(D7=A+(B*C7)+(C*((C7)^2)))
8	_____	(D8=A+(B*C8)+(C*((C8)^2)))
9	_____	(D9=A+(B*C9)+(C*((C9)^2)))
10		
11		
12	*VOLTAGE READING FROM	*THIS FORMULA RELATES TOC
13	BECKMAN MODEL 915-B	TO % FULLSCALE VOLTAGE
14	TOC ANALYZER (0-100 UNITS)	A, B, C: CONSTANTS FROM LEAST
15		SQUARES ANALYSIS OF
16		CALIBRATION DATA
17		
18		
19		
20		
21		
22		
23		
24		
25		
26		
27		
28		
29		
30		

	E	F	G
1	Dilution *	TOC (mg C/L)	Balance Factor *
2	_____	(D2*E2)	4
3	_____	(D3*E3)	4
4	_____	(D4*E4)	0.5
5	_____	(D5*E5)	0.5
6	_____	(D6*E6)	6
7	_____	(D7*E7)	0.125
8	_____	(D8*E8)	0.125
9	_____	(D9*E9)	0.3125
10		(F2-F3)	4
11			
12	*SAMPLE DILUTION REQUIRED		*SAMPLE VOLUME
13	TO DETERMINE TOC OVER A 0-250		IN LITERS
14	PPM TOC RANGE		
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			

	H	I	J	K
1	mg Carbon	mmoles C	ug Cl	blank
2	(F2*G2)	(H2/12)	_____	_____
3	(F3*G3)	(H3/12)	_____	_____
4	(F4*G4)	(H4/12)	_____	_____
5	(F5*G5)	(H5/12)	_____	_____
6	(F6*G6)	(H6/12)	_____	_____
7	(F7*G7)	(H7/12)	_____	_____
8	(F8*G8)	(H8/12)	_____	_____
9	(F9*G9)	(H9/12)	_____	_____
10	(F10*G10)	(H10/12)		
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				
27				
28				
29				
30				

	L	M
1	AOX (dilution)	Dilution *
2	((J2-K2)/0.1)	_____
3	((J3-K3)/0.1)	_____
4	((J4-K4)/0.1)	_____
5	((J5-K5)/0.1)	_____
6	((J6-K6)/0.1)	_____
7	((J7-K7)/0.1)	_____
8	((J8-K8)/0.1)	_____
9	((J9-K9)/0.1)	_____
10		
11		
12		*SAMPLE DILUTION REQUIRED
13		TO DETERMINE AOX OVER A
14		0-20 MICROGRAM AOX RANGE
15		
16		
17		
18		
19		
20		
21		
22		
23		
24		
25		
26		
27		
28		
29		
30		

	N	O	P	Q
1	AOX (ug/L sample)	mg Cl	mmoles Cl	C/Cl
2	(L2*M2)	(N2*(G2/1000))	(O2/35.5)	(I2/P2)
3	(L3*M3)	(N3*(G3/1000))	(O3/35.5)	(I3/P3)
4	(L4*M4)	(N4*(G4/1000))	(O4/35.5)	(I4/P4)
5	(L5*M5)	(N5*(G5/1000))	(O5/35.5)	(I5/P5)
6	(L6*M6)	(N6*(G6/1000))	(O6/35.5)	(I6/P6)
7	(L7*M7)	(N7*(G7/1000))	(O7/35.5)	(I7/P7)
8	(L8*M8)	(N8*(G8/1000))	(O8/35.5)	(I8/P8)
9	(L9*M9)	(N9*(G9/1000))	(O9/35.5)	(I9/P9)
10		(O2-O3)	(O10/35.5)	(I10/P10)
11				
12				
13				
14				
15				
16				
17				
18				
19				
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22				
23				
24				
25				
26				
27				
28				
29				
30				

	R	S	T	U
1	Effluent:	_____		
2	Type:	_____		
3	Fraction	mg C	mM C	mg Cl
4	Whole	(H2)	(I2)	(O2)
5	NVW	(H3)	(I3)	(O3)
6	NVEE I	(H4)	(I4)	(O4)
7	NVEE II	(H5)	(I5)	(O5)
8	NVNEE	(H6)	(I6)	(O6)
9	NVEEA	(H7)	(I7)	(O7)
10	NVEEP	(H8)	(I8)	(O8)
11	NVEEN	(H9)	(I9)	(O9)
12	Volatiles	(H10)	(I10)	(O10)
13				
14			(g)	(kg)
15	Dry Pulp Weight:		_____	(T15/1000)
16				
17	Effluent Volume Extracted (L):			
18	Total Effluent Volume (L):			
19				
20				mg C
21	Overall Balance:			(S6+S7+S8)
22	% Recovered			((U21/S5)*100)
23	Ether Ext. Balance:			(S9+S10+S11)
24	% Recovered			((U23/S6)*100)
25				
26				
27				
28				
29				
30				

	V	W
1		
2		
3	mM Cl	C/Cl
4	(P2)	(Q2)
5	(P3)	(Q3)
6	(P4)	(Q4)
7	(P5)	(Q5)
8	(P6)	(Q6)
9	(P7)	(Q7)
10	(P8)	(Q8)
11	(P9)	(Q9)
12	(P10)	(Q10)
13		
14	(tonne)	
15	(U15/1000)	
16		
17	_____ (L)	
18	_____ (L)	
19		
20	mg Cl	kg C/bdtp
21	(U6+U7+U8)	(X6+X7+X8)
22	((V21/U5)*100)	((W21/X5)*100)
23	(U9+U10+U11)	(X9+X10+X11)
24	((V23/U6)*100)	((W23/X6)*100)
25		
26		
27		
28		
29		
30		

X

1	
2	Carbon
3	(kg/bdtp)
4	(((H2/1000000)*(V18/V17))/V15)
5	(((H3/1000000)*(V18/V17))/V15)
6	(((H4/1000000)*(V18/V17))/V15)
7	(((H5/1000000)*(V18/V17))/V15)
8	(((H6/1000000)*(V18/V17))/V15)
9	(((H7/1000000)*(V18/V17))/V15)
10	(((H8/1000000)*(V18/V17))/V15)
11	(((H9/1000000)*(V18/V17))/V15)
12	(((H10/1000000)*(V18/V17))/V15)
13	
14	
15	
16	
17	
18	
19	
20	kg Cl/bdtp
21	(Y6+Y7+Y8)
22	((X21/Y5)*100)
23	(Y9+Y10+Y11)
24	((X23/Y6)*100)
25	
26	
27	
28	
29	
30	

Y

```
1
2          Chlorine
3          (kg/bdtp)
4          (((O2/1000000)*(V18/V17))/V15)
5          (((O3/1000000)*(V18/V17))/V15)
6          (((O4/1000000)*(V18/V17))/V15)
7          (((O5/1000000)*(V18/V17))/V15)
8          (((O6/1000000)*(V18/V17))/V15)
9          (((O7/1000000)*(V18/V17))/V15)
10         (((O8/1000000)*(V18/V17))/V15)
11         (((O9/1000000)*(V18/V17))/V15)
12         (((O10/1000000)*(V18/V17))/V15)
13
14
15
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Appendix 7B: Instructions

This Lotus spreadsheet was written and used to perform the routine transformation of AOX and TOC data to molar chlorine to carbon ratios, and to calculate mass balances around the ether extraction and extract fractionation stages.

The identification code of the effluent is entered in cell A2 of the spreadsheet. Cells B2-B10 list the names of all effluent fractions. Rows 2-10 correspond to these named effluent fractions for columns B through Q of the spreadsheet.

The % fullscale voltage readings from the Beckman model 915-B TOC analyzer, for the effluent fractions corresponding to cells B2-B9, are entered into cells C2-C9. A value for the volatile fraction is not entered since this fraction is determined by difference between the whole and NVW fractions.

The TOC calibration formula is entered into Cells D2-D9. The formula calculates the TOC of the sample from the % fullscale voltage readings, and displays the results in cells D2-D9. The quadratic calibration formula is given in column D with variables in place of the formula constants. Constants for the calibration formula are determined from the calibration data using a least squares computer program. Column D gives the TOC concentration of the diluted effluent fraction that is used for TOC analysis.

The dilution factors used during the TOC measurement of effluent fractions are entered into cells E2-E9. For TOC analysis over the 0-250 ppm calibration range, the sample dilution is often 1:1 (entered as 1 in the spreadsheet). In some cases 2:1 or 4:1 dilutions are used (entered as 2 or 4). The formulas in column F calculate the TOC content of each undiluted effluent fraction. Here the volatile TOC (row 10) is calculated by difference.

The total effective volumes of all fractions are given in column G. These "balance factors" are calculated as follows:

$$\text{Balance Factor} = V_s(V_f/V_{fs})$$

where

V_s = AOX or TOC sample volume (L)
V_f = total effluent fraction volume (L)
V_{fs} = volume of the fraction used to prepare the AOX or TOC sample (L)

These factors are required to determine mass balances, since AOX and TOC samples are prepared from only part of the total effluent fraction. For example, the ether extracts are 0.5 L samples. However, only 0.1 L of the ether is used for AOX and TOC determinations because the remaining ether is fractionated. Therefore, the portion of the sample that is used contains only 20% of the TOC or AOX, and the resulting quantity of TOC or AOX is multiplied by 5 (or divided by 0.2) to correct the value so that all TOC or AOX in the fraction is included in the balances. In this case the Balance Factor = 0.1 L(0.5 L/0.1 L) = 0.5 L.

In the case of the extract subfractions the balance factors are more complex. AOX or TOC sample volume is 0.1 L for the NVEEA and NVEEP fractions. But only 0.4 L of the 0.5 L of ether is fractionated. These subfractions therefore contain only 80% of the material that the total volume of ether contained, and the balance factors correct for this omission. In these cases the Balance Factor = 0.1 L(0.5 L/0.4 L) = 0.125 L. This is equivalent to dividing the TOC or AOX in the 0.1 L sample by 0.8 (to correct for only 80% of the original ether use). Similarly the balance factor for the 0.25 L NVEEN sample = 0.25 L(0.5 L/0.4 L) = 0.3125 L.

The formulas in column H calculate the total quantity of TOC in each effluent fraction. This is done by multiplying the concentration of the effluent fraction by the balance factor. The formulas in column I calculate the total millimoles of carbon in each effluent fraction. These values are used later in the TOC balances.

The determined AOX values for each effluent fraction (in μg Cl) that corresponds to cells B2-B9, are entered into cells J2-J9. The AOX blank values (in μg Cl) associated with the determined AOX values are entered into cells K2-K9. The formulas in column L calculate the AOX concentration in μg/L for each 0.1 L AOX sample.

The dilution factors used on the effluent fraction AOX determinations are entered in column M, and vary from 2:1 (entered as 2) to 2000:1 (entered as 2000) depending on the bleaching conditions and on the type of fraction. All fractions are diluted such that 0.1 L of the dilution contains no more than 20 μg of AOX. The formulas in column N calculate the AOX concentration in the undiluted fractions using the AOX values of the dilutions and the corresponding dilution factors.

The formulas in column O calculate the quantity (in mg) of AOX in each effluent fraction, using the column N AOX concentrations and the column G balance factors. Volatile AOX is determined by difference. The formulas in column P calculate the number of millimoles of organic chlorine (AOX) in each effluent fraction. In column Q, the molar ratios of carbon to chlorine are calculated for each effluent fraction.

Columns R through Y are the output portion of the spreadsheet, in which the molar carbon to chlorine ratios and AOX and TOC mass balances are displayed. The output results of this spreadsheet are given in Appendix 8 for all fractionation studies done during this research.

The effluent code and a description of the effluent may be entered in cells S1 and S2. In addition to displaying the mg and millimoles (mM) of carbon and mg and mM of chlorine in each effluent fraction and the ratio of carbon to chlorine atoms, this part of the spreadsheet also expresses the results in terms of kg of carbon or chlorine per ton (1000 kg) of "bone dry" pulp. To express results in these terms, several other values must be entered into the spreadsheet, including the dry pulp weight in grams (cell T15), the vol-

ume of effluent (L) that is extracted with ether (cell V17), and the total volume of effluent (L) produced by the bleaching experiment (cell V18). The formulas in columns X and Y calculate the carbon and chlorine contents of all fractions in terms of kg/ton of pulp.

The formulas in cells R21-X24 calculate the carbon and chlorine mass balances around the ether extraction and the extract fractionation scheme, and give the percentage recovery in each case. Overall AOX or TOC balances (rows 21-22) are given by the sum of the NVEE I, NVEE II, and NVNEE fraction AOX or TOC. Overall AOX or TOC recovery is given by the overall balance value expressed as a percentage of the NVW fraction AOX or TOC. The balances around the ether extract fractionation (rows 23-24) are given by the sum of the NVEEA, NVEEP, and NVEEN fraction AOX or TOC. Recovery is given by the fractionation balance AOX or TOC expressed as a percentage of NVEE I fraction AOX or TOC.

APPENDIX 8: FRACTIONATION DATA

Appendix 8A: Effluent Data

Effluent: DC4146-36
Type: 100% D (lab)

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	3.28E+02	2.73E+01	2.55E+01	7.18E-01	3.80E+01	3.85E+00	2.99E-01
NVW	2.95E+02	2.46E+01	2.09E+01	5.90E-01	4.17E+01	3.47E+00	2.46E-01
NVEE I	3.26E+01	2.71E+00	4.65E+00	1.31E-01	2.07E+01	3.83E-01	5.47E-02
NVEE II	1.92E+01	1.60E+00	3.78E+00	1.07E-01	1.50E+01	2.26E-01	4.45E-02
NVNEE	2.92E+02	2.43E+01	1.22E+01	3.45E-01	7.05E+01	3.43E+00	1.44E-01
NVEEA	2.69E+01	2.24E+00	4.35E+00	1.23E-01	1.83E+01	3.16E-01	5.11E-02
NVEEP	2.03E+00	1.70E-01	2.17E-01	6.11E-03	2.78E+01	2.39E-02	2.55E-03
NVEEN	4.69E+00	3.91E-01	1.31E-01	3.68E-03	1.06E+02	5.51E-02	1.53E-03
Volatile	3.24E+01	2.70E+00	4.54E+00	1.28E-01	2.11E+01	3.80E-01	5.33E-02

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.41E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	3.44E+02	2.07E+01	4.04E+00	2.43E-01
% Recovered	1.16E+02	9.87E+01	1.16E+02	9.87E+01
Ether Ext. Balance:	3.37E+01	4.70E+00	3.95E-01	5.52E-02
% Recovered	1.03E+02	1.01E+02	1.03E+02	1.01E+02

Effluent: E14146-36
Type: Eo after 100% D (lab)

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	5.55E+02	4.62E+01	8.25E+00	2.32E-01	1.99E+02	6.79E+00	1.01E-01
NVW	5.21E+02	4.35E+01	7.81E+00	2.20E-01	1.98E+02	6.39E+00	9.57E-02
NVEE I	3.31E+01	2.76E+00	1.04E+00	2.92E-02	9.45E+01	4.06E-01	1.27E-02
NVEE II	3.25E+01	2.71E+00	2.72E-01	7.66E-03	3.54E+02	3.99E-01	3.33E-03
NVNEE	4.49E+02	3.74E+01	5.94E+00	1.67E-01	2.23E+02	5.50E+00	7.28E-02
NVEEA	2.48E+01	2.07E+00	6.99E-01	1.97E-02	1.05E+02	3.04E-01	8.56E-03
NVEEP	2.97E+00	2.48E-01	1.98E-01	5.58E-03	4.43E+01	3.64E-02	2.43E-03
NVEEN	4.17E+00	3.48E-01	1.05E-01	2.96E-03	1.17E+02	5.11E-02	1.29E-03
Volatile	3.31E+01	2.76E+00	4.40E-01	1.24E-02	2.22E+02	4.05E-01	5.39E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.47E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	5.14E+02	7.25E+00	6.30E+00	8.88E-02
% Recovered	9.86E+01	9.28E+01	9.86E+01	9.28E+01
Ether Ext. Balance:	3.20E+01	1.00E+00	3.92E-01	1.23E-02
% Recovered	9.65E+01	9.66E+01	9.65E+01	9.66E+01

Effluent: DC4146-48
Type: 100% D (lab)

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	3.24E+02	2.70E+01	2.50E+01	7.04E-01	3.83E+01	3.80E+00	2.94E-01
NVW	2.90E+02	2.42E+01	2.38E+01	6.71E-01	3.60E+01	3.41E+00	2.80E-01
NVEE I	2.27E+01	1.90E+00	3.73E+00	1.05E-01	1.80E+01	2.67E-01	4.39E-02
NVEE II	2.11E+01	1.76E+00	4.27E+00	1.20E-01	1.46E+01	2.48E-01	5.02E-02
NVNEE	3.14E+02	2.62E+01	1.36E+01	3.84E-01	6.82E+01	3.69E+00	1.60E-01
NVEEA	2.06E+01	1.71E+00	3.14E+00	8.85E-02	1.94E+01	2.42E-01	3.69E-02
NVEEP	1.68E+00	1.40E-01	1.71E-01	4.83E-03	2.90E+01	1.98E-02	2.01E-03
NVEEN	3.89E+00	3.24E-01	1.26E-01	3.54E-03	9.16E+01	4.57E-02	1.48E-03
Volatile	3.37E+01	2.81E+00	1.16E+00	3.27E-02	8.59E+01	3.96E-01	1.36E-02

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.41E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	3.58E+02	2.17E+01	4.21E+00	2.54E-01
% Recovered	1.23E+02	9.09E+01	1.23E+02	9.09E+01
Ether Ext. Balance:	2.61E+01	3.44E+00	3.07E-01	4.04E-02
% Recovered	1.15E+02	9.20E+01	1.15E+02	9.20E+01

Effluent: E14146-49
Type: Eo after 100% D (lab)

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	5.39E+02	4.49E+01	8.34E+00	2.35E-01	1.91E+02	6.60E+00	1.02E-01
NVW	5.17E+02	4.31E+01	7.94E+00	2.24E-01	1.93E+02	6.33E+00	9.73E-02
NVEE I	3.26E+01	2.72E+00	1.02E+00	2.87E-02	9.47E+01	3.99E-01	1.25E-02
NVEE II	3.22E+01	2.69E+00	2.29E-01	6.44E-03	4.17E+02	3.95E-01	2.80E-03
NVNEE	4.45E+02	3.71E+01	6.08E+00	1.71E-01	2.17E+02	5.45E+00	7.45E-02
NVEEA	2.62E+01	2.19E+00	6.75E-01	1.90E-02	1.15E+02	3.21E-01	8.27E-03
NVEEP	2.79E+00	2.32E-01	1.47E-01	4.15E-03	5.60E+01	3.41E-02	1.80E-03
NVEEN	3.92E+00	3.27E-01	5.72E-02	1.61E-03	2.03E+02	4.80E-02	7.01E-04
Volatile	2.21E+01	1.85E+00	4.00E-01	1.13E-02	1.64E+02	2.71E-01	4.90E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.47E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	5.10E+02	7.32E+00	6.25E+00	8.97E-02
% Recovered	9.86E+01	9.22E+01	9.86E+01	9.22E+01
Ether Ext. Balance:	3.29E+01	8.79E-01	4.04E-01	1.08E-02
% Recovered	1.01E+02	8.64E+01	1.01E+02	8.64E+01

Effluent: DC4146-61
Type: 100% Cl (lab)

Fraction	mg C	mM C	mg Cl	mM Cl^-	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	5.24E+02	4.36E+01	2.34E+02	6.60E+00	6.61E+00	6.15E+00	2.75E+00
NVW	4.29E+02	3.58E+01	2.09E+02	5.88E+00	6.08E+00	5.04E+00	2.45E+00
NVEE I	5.79E+01	4.83E+00	6.72E+01	1.89E+00	2.55E+00	6.81E-01	7.90E-01
NVFE II	4.54E+01	3.78E+00	5.37E+00	1.51E-01	2.50E+01	5.33E-01	6.32E-02
NVNEE	4.08E+02	3.40E+01	1.14E+02	3.22E+00	1.05E+01	4.80E+00	1.34E+00
NVEEA	3.83E+01	3.19E+00	3.88E+01	1.09E+00	2.92E+00	4.50E-01	4.56E-01
NVEEP	9.20E+00	7.67E-01	7.96E+00	2.24E-01	3.42E+00	1.08E-01	9.35E-02
NVEEN	3.34E+00	2.79E-01	5.03E-01	1.42E-02	1.97E+01	3.93E-02	5.91E-03
Volatile	9.44E+01	7.87E+00	2.56E+01	7.21E-01	1.09E+01	1.11E+00	3.01E-01

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.41E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	5.11E+02	1.87E+02	6.01E+00	2.20E+00
% Recovered	1.19E+02	8.96E+01	1.19E+02	8.96E+01
Ether Ext. Balance:	5.09E+01	4.73E+01	5.98E-01	5.56E-01
% Recovered	8.78E+01	7.04E+01	8.78E+01	7.04E+01

Effluent: E14146-61
Type: Eo after 100% Cl (lab)

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	7.65E+02	6.38E+01	6.47E+01	1.82E+00	3.50E+01	9.37E+00	7.93E-01
NVW	6.89E+02	5.74E+01	6.38E+01	1.80E+00	3.19E+01	8.44E+00	7.82E-01
NVEE I	1.08E+02	8.97E+00	1.41E+01	3.98E-01	2.25E+01	1.32E+00	1.73E-01
NVEE II	8.55E+01	7.13E+00	2.35E+00	6.62E-02	1.08E+02	1.05E+00	2.88E-02
NVNEE	5.45E+02	4.54E+01	4.33E+01	1.22E+00	3.72E+01	6.67E+00	5.31E-01
NVEEA	8.29E+01	6.91E+00	1.15E+01	3.23E-01	2.14E+01	1.02E+00	1.40E-01
NVEEP	7.22E+00	6.01E-01	1.81E+00	5.09E-02	1.18E+01	8.84E-02	2.21E-02
NVEEN	5.48E+00	4.56E-01	4.24E-01	1.19E-02	3.82E+01	6.71E-02	5.20E-03
Volatile	7.64E+01	6.36E+00	8.80E-01	2.48E-02	2.57E+02	9.35E-01	1.08E-02

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.47E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	7.38E+02	5.98E+01	9.04E+00	7.33E-01
% Recovered	1.07E+02	9.37E+01	1.07E+02	9.37E+01
Ether Ext. Balance:	9.56E+01	1.37E+01	1.17E+00	1.68E-01
% Recovered	8.88E+01	9.69E+01	8.88E+01	9.69E+01

Effluent: DC4146-82
Type: 100% Cl (lab)

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	5.41E+02	4.51E+01	2.18E+02	6.14E+00	7.35E+00	6.36E+00	2.56E+00
NVW	4.82E+02	4.01E+01	2.02E+02	5.69E+00	7.06E+00	5.66E+00	2.37E+00
NVEE I	7.08E+01	5.90E+00	5.38E+01	1.51E+00	3.90E+00	8.32E-01	6.32E-01
NVEE II	1.87E+01	1.56E+00	4.08E+00	1.15E-01	1.36E+01	2.20E-01	4.79E-02
NVNEE	5.53E+02	4.61E+01	1.16E+02	3.27E+00	1.41E+01	6.50E+00	1.37E+00
NVEEA	4.66E+01	3.88E+00	3.66E+01	1.03E+00	3.77E+00	5.48E-01	4.30E-01
NVEEP	1.05E+01	8.75E-01	7.40E+00	2.08E-01	4.20E+00	1.23E-01	8.69E-02
NVEEN	6.38E+00	5.32E-01	5.35E-01	1.51E-02	3.53E+01	7.50E-02	6.29E-03
Volatile	5.96E+01	4.96E+00	1.58E+01	4.45E-01	1.12E+01	7.00E-01	1.86E-01

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.41E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	6.43E+02	1.74E+02	7.55E+00	2.05E+00
% Recovered	1.33E+02	8.62E+01	1.33E+02	8.62E+01
Ether Ext. Balance:	6.35E+01	4.45E+01	7.46E-01	5.23E-01
% Recovered	8.96E+01	8.28E+01	8.96E+01	8.28E+01

Effluent: E14146-82
Type: Eo after 100% Cl (lab)

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	8.29E+02	6.91E+01	7.01E+01	1.97E+00	3.50E+01	1.02E+01	8.58E-01
NVW	7.64E+02	6.37E+01	6.11E+01	1.72E+00	3.70E+01	9.36E+00	7.49E-01
NVEE I	1.11E+02	9.28E+00	1.26E+01	3.55E-01	2.61E+01	1.36E+00	1.54E-01
NVEE II	5.80E+01	4.83E+00	2.65E+00	7.48E-02	6.46E+01	7.11E-01	3.25E-02
NVNEE	7.25E+02	6.04E+01	4.85E+01	1.37E+00	4.42E+01	8.88E+00	5.94E-01
NVEEA	8.54E+01	7.12E+00	1.11E+01	3.11E-01	2.29E+01	1.05E+00	1.35E-01
NVEEP	5.92E+00	4.93E-01	7.55E-01	2.13E-02	2.32E+01	7.25E-02	9.24E-03
NVEEN	5.52E+00	4.60E-01	4.19E-01	1.18E-02	3.90E+01	6.76E-02	5.13E-03
Volatile	6.51E+01	5.42E+00	8.96E+00	2.52E-01	2.15E+01	7.97E-01	1.10E-01

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.47E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	8.94E+02	6.37E+01	1.10E+01	7.81E-01
% Recovered	1.17E+02	1.04E+02	1.17E+02	1.04E+02
Ether Ext. Balance:	9.69E+01	1.22E+01	1.19E+00	1.50E-01
% Recovered	8.70E+01	9.71E+01	8.70E+01	9.71E+01

Effluent: DC4146-94
Type: 100% ClO2 (lab), Non-O2 pulp

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	6.24E+02	5.20E+01	4.70E+01	1.32E+00	3.93E+01	7.33E+00	5.52E-01
NVW	5.33E+02	4.44E+01	4.58E+01	1.29E+00	3.45E+01	6.27E+00	5.38E-01
NVEE I	4.27E+01	3.56E+00	6.39E+00	1.80E-01	1.98E+01	5.01E-01	7.51E-02
NVEE II	7.06E+01	5.88E+00	7.50E+00	2.11E-01	2.78E+01	8.29E-01	8.82E-02
NVNEE	4.60E+02	3.84E+01	2.37E+01	6.68E-01	5.75E+01	5.41E+00	2.78E-01
NVEEA	3.68E+01	3.06E+00	4.77E+00	1.35E-01	2.28E+01	4.32E-01	5.61E-02
NVEEP	3.93E+00	3.28E-01	5.81E-01	1.64E-02	2.00E+01	4.62E-02	6.83E-03
NVEEN	6.67E+00	5.56E-01	2.91E-01	8.20E-03	6.77E+01	7.84E-02	3.42E-03
Volatile	9.09E+01	7.58E+00	1.20E+00	3.38E-02	2.24E+02	1.07E+00	1.41E-02

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.41E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	5.74E+02	3.76E+01	6.74E+00	4.42E-01
% Recovered	1.08E+02	8.22E+01	1.08E+02	8.22E+01
Ether Ext. Balance:	4.74E+01	5.65E+00	5.57E-01	6.64E-02
% Recovered	1.11E+02	8.84E+01	1.11E+02	8.84E+01

Effluent: E14146-94
Type: Eo after 100% ClO2 (lab), Non-O2

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	1.39E+03	1.16E+02	2.78E+01	7.84E-01	1.48E+02	1.71E+01	3.41E-01
NVW	1.34E+03	1.12E+02	2.73E+01	7.69E-01	1.45E+02	1.64E+01	3.34E-01
NVEE I	5.41E+01	4.51E+00	2.23E+00	6.27E-02	7.19E+01	6.63E-01	2.73E-02
NVEE II	7.01E+01	5.84E+00	1.02E+00	2.86E-02	2.04E+02	8.58E-01	1.24E-02
NVNEE	1.10E+03	9.13E+01	2.26E+01	6.35E-01	1.44E+02	1.34E+01	2.76E-01
NVEEA	4.29E+01	3.58E+00	1.57E+00	4.42E-02	8.08E+01	5.26E-01	1.92E-02
NVEEP	6.69E+00	5.58E-01	5.69E-01	1.60E-02	3.48E+01	8.20E-02	6.97E-03
NVEEN	5.59E+00	4.66E-01	2.24E-01	6.32E-03	7.38E+01	6.85E-02	2.75E-03
Volatile	5.33E+01	4.44E+00	5.40E-01	1.52E-02	2.92E+02	6.53E-01	6.61E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.47E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	1.22E+03	2.58E+01	1.49E+01	3.16E-01
% Recovered	9.10E+01	9.45E+01	9.10E+01	9.45E+01
Ether Ext. Balance:	5.52E+01	2.36E+00	6.76E-01	2.90E-02
% Recovered	1.02E+02	1.06E+02	1.02E+02	1.06E+02

Effluent: DC4146-113
Type: 100% ClO2 (lab), Non-O2 pulp

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	6.16E+02	5.13E+01	5.06E+01	1.42E+00	3.60E+01	7.23E+00	5.94E-01
NVW	5.49E+02	4.57E+01	4.34E+01	1.22E+00	3.74E+01	6.45E+00	5.09E-01
NVEE I	3.55E+01	2.96E+00	6.17E+00	1.74E-01	1.70E+01	4.18E-01	7.25E-02
NVEE II	6.12E+01	5.10E+00	6.00E+00	1.69E-01	3.02E+01	7.19E-01	7.05E-02
NVNEE	5.15E+02	4.29E+01	2.83E+01	7.98E-01	5.38E+01	6.05E+00	3.33E-01
NVEEA	3.08E+01	2.56E+00	4.55E+00	1.28E-01	2.00E+01	3.61E-01	5.35E-02
NVEEP	3.69E+00	3.08E-01	5.12E-01	1.44E-02	2.13E+01	4.34E-02	6.02E-03
NVEEN	4.96E+00	4.13E-01	3.29E-01	9.27E-03	4.46E+01	5.83E-02	3.87E-03
Volatile	6.68E+01	5.56E+00	7.20E+00	2.03E-01	2.74E+01	7.85E-01	8.46E-02

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.41E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	6.12E+02	4.05E+01	7.19E+00	4.76E-01
% Recovered	1.11E+02	9.34E+01	1.11E+02	9.34E+01
Ether Ext. Balance:	3.94E+01	5.39E+00	4.63E-01	6.34E-02
% Recovered	1.11E+02	8.74E+01	1.11E+02	8.74E+01

Effluent: E14146-114
Type: Eo after 100% ClO2 (lab), Non-O2

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	1.28E+03	1.07E+02	2.52E+01	7.10E-01	1.50E+02	1.57E+01	3.09E-01
NVW	1.22E+03	1.02E+02	2.47E+01	6.95E-01	1.47E+02	1.50E+01	3.02E-01
NVEE I	4.43E+01	3.69E+00	1.79E+00	5.06E-02	7.30E+01	5.42E-01	2.20E-02
NVEE II	6.03E+01	5.03E+00	1.11E+00	3.12E-02	1.61E+02	7.39E-01	1.36E-02
NVNEE	1.03E+03	8.62E+01	2.06E+01	5.80E-01	1.49E+02	1.27E+01	2.52E-01
NVEEA	4.01E+01	3.34E+00	1.75E+00	4.93E-02	6.78E+01	4.91E-01	2.14E-02
NVEEP	8.72E+00	7.27E-01	5.96E-01	1.68E-02	4.33E+01	1.07E-01	7.30E-03
NVEEN	1.12E+01	9.34E-01	4.04E-01	1.14E-02	8.21E+01	1.37E-01	4.95E-03
Volatile	5.77E+01	4.81E+00	5.20E-01	1.46E-02	3.28E+02	7.06E-01	6.37E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.47E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	1.14E+03	2.35E+01	1.40E+01	2.88E-01
% Recovered	9.32E+01	9.51E+01	9.32E+01	9.51E+01
Ether Ext. Balance:	6.00E+01	2.75E+00	7.35E-01	3.37E-02
% Recovered	1.36E+02	1.53E+02	1.36E+02	1.53E+02

Effluent:	DC4146-125						
Type:	100% ClO2 (lab),pre-O2 pulp,pH 4					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	4.57E+02	3.81E+01	3.25E+01	9.14E-01	4.16E+01	5.37E+00	3.81E-01
NVW	4.33E+02	3.61E+01	2.69E+01	7.57E-01	4.77E+01	5.09E+00	3.16E-01
NVEE I	5.47E+01	4.56E+00	6.57E+00	1.85E-01	2.46E+01	6.43E-01	7.73E-02
NVEE II	3.29E+01	2.74E+00	4.24E+00	1.19E-01	2.29E+01	3.86E-01	4.98E-02
NVNEE	3.61E+02	3.01E+01	1.30E+01	3.65E-01	8.24E+01	4.25E+00	1.52E-01
NVEEA	3.65E+01	3.04E+00	5.33E+00	1.50E-01	2.02E+01	4.28E-01	6.27E-02
NVEEP	2.77E+00	2.30E-01	2.32E-01	6.54E-03	3.52E+01	3.25E-02	2.73E-03
NVEEN	1.49E+01	1.24E+00	2.98E-01	8.40E-03	1.47E+02	1.75E-01	3.50E-03
Volatile	2.35E+01	1.95E+00	5.60E+00	1.58E-01	1.24E+01	2.76E-01	6.58E-02

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.41E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	4.49E+02	2.38E+01	5.28E+00	2.80E-01
% Recovered	1.04E+02	8.86E+01	1.04E+02	8.86E+01
Ether Ext. Balance:	5.41E+01	5.86E+00	6.35E-01	6.89E-02
% Recovered	9.89E+01	8.92E+01	9.89E+01	8.92E+01

Effluent:	E14146-125						
Type:	Eo, 100% ClO2 (lab), pre-O2,pH 4					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	5.72E+02	4.77E+01	7.70E+00	2.17E-01	2.20E+02	7.01E+00	9.43E-02
NVW	5.44E+02	4.53E+01	6.92E+00	1.95E-01	2.32E+02	6.66E+00	8.48E-02
NVEE I	4.34E+01	3.62E+00	1.22E+00	3.44E-02	1.05E+02	5.32E-01	1.50E-02
NVEE II	2.58E+01	2.15E+00	2.20E-01	6.20E-03	3.47E+02	3.16E-01	2.69E-03
NVNEE	4.77E+02	3.97E+01	5.83E+00	1.64E-01	2.42E+02	5.84E+00	7.14E-02
NVEEA	2.78E+01	2.31E+00	8.55E-01	2.41E-02	9.61E+01	3.40E-01	1.05E-02
NVEEP	4.18E+00	3.49E-01	1.76E-01	4.96E-03	7.03E+01	5.13E-02	2.16E-03
NVEEN	7.22E+00	6.02E-01	1.65E-01	4.65E-03	1.29E+02	8.85E-02	2.02E-03
Volatile	2.87E+01	2.39E+00	7.80E-01	2.20E-02	1.09E+02	3.52E-01	9.56E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.47E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	5.46E+02	7.27E+00	6.69E+00	8.90E-02
% Recovered	1.00E+02	1.05E+02	1.00E+02	1.05E+02
Ether Ext. Balance:	3.92E+01	1.20E+00	4.80E-01	1.47E-02
% Recovered	9.03E+01	9.78E+01	9.03E+01	9.78E+01

Effluent:	DC4146-136						
Type:	100% ClO2 (lab),pre-O2 pulp,pH 4					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	4.40E+02	3.66E+01	3.29E+01	9.26E-01	3.96E+01	5.17E+00	3.86E-01
NVW	3.88E+02	3.23E+01	2.81E+01	7.92E-01	4.08E+01	4.56E+00	3.30E-01
NVEE I	1.26E+02	1.05E+01	4.03E+00	1.14E-01	9.24E+01	1.48E+00	4.74E-02
NVEE II	7.22E+01	6.02E+00	2.86E+00	8.06E-02	7.47E+01	8.48E-01	3.36E-02
NVNEE	4.08E+02	3.40E+01	1.76E+01	4.94E-01	6.87E+01	4.79E+00	2.06E-01
NVEEA	2.56E+01	2.13E+00	2.98E+00	8.38E-02	2.55E+01	3.01E-01	3.50E-02
NVEEP	3.31E+00	2.76E-01	2.03E-01	5.72E-03	4.83E+01	3.89E-02	2.39E-03
NVEEN	4.11E+00	3.42E-01	2.47E-01	6.95E-03	4.93E+01	4.83E-02	2.90E-03
Volatile	5.18E+01	4.32E+00	4.74E+00	1.34E-01	3.24E+01	6.09E-01	5.57E-02

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.41E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	6.06E+02	2.44E+01	7.12E+00	2.87E-01
% Recovered	1.56E+02	8.69E+01	1.56E+02	8.69E+01
Ether Ext. Balance:	3.30E+01	3.42E+00	3.88E-01	4.02E-02
% Recovered	2.63E+01	8.50E+01	2.63E+01	8.50E+01

Effluent:	E14146-137						
Type:	Eo, 100% ClO2 (lab), pre-O2,pH 4					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	5.34E+02	4.45E+01	7.58E+00	2.14E-01	2.08E+02	6.54E+00	9.29E-02
NVW	5.02E+02	4.19E+01	7.04E+00	1.98E-01	2.11E+02	6.15E+00	8.62E-02
NVEE I	6.11E+01	5.09E+00	1.25E+00	3.54E-02	1.44E+02	7.48E-01	1.54E-02
NVEE II	3.46E+01	2.88E+00	1.84E-01	5.20E-03	5.55E+02	4.24E-01	2.26E-03
NVNEE	5.00E+02	4.17E+01	5.26E+00	1.48E-01	2.81E+02	6.13E+00	6.44E-02
NVEEA	4.72E+01	3.93E+00	9.40E-01	2.65E-02	1.49E+02	5.78E-01	1.15E-02
NVEEP	4.10E+00	3.41E-01	1.45E-01	4.08E-03	8.37E+01	5.02E-02	1.77E-03
NVEEN	2.55E+00	2.13E-01	9.31E-02	2.62E-03	8.11E+01	3.13E-02	1.14E-03
Volatile	3.14E+01	2.61E+00	5.40E-01	1.52E-02	1.72E+02	3.84E-01	6.62E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.47E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	5.96E+02	6.70E+00	7.30E+00	8.21E-02
% Recovered	1.19E+02	9.51E+01	1.19E+02	9.51E+01
Ether Ext. Balance:	5.38E+01	1.18E+00	6.60E-01	1.44E-02
% Recovered	8.82E+01	9.39E+01	8.82E+01	9.39E+01

Effluent:	DC4146-149					
Type:	100% ClO2 (lab),pre-O2 pulp,30 min				Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl⁻	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	3.59E+02	2.99E+01	2.61E+01	7.35E-01	4.07E+01	4.85E+00	3.52E-01
NVW	3.24E+02	2.70E+01	2.07E+01	5.84E-01	4.62E+01	4.37E+00	2.80E-01
NVEE I	4.55E+01	3.79E+00	7.07E+00	1.99E-01	1.90E+01	6.14E-01	9.54E-02
NVEE II	1.90E+01	1.58E+00	2.78E+00	7.83E-02	2.02E+01	2.56E-01	3.75E-02
NVNEE	2.50E+02	2.08E+01	1.11E+01	3.12E-01	6.67E+01	3.37E+00	1.49E-01
NVEEA	4.05E+01	3.38E+00	7.06E+00	1.99E-01	1.70E+01	5.47E-01	9.53E-02
NVEEP	2.19E+00	1.83E-01	2.45E-01	6.89E-03	2.65E+01	2.96E-02	3.30E-03
NVEEN	1.18E+01	9.81E-01	2.23E-01	6.28E-03	1.56E+02	1.59E-01	3.01E-03
Volatile	3.52E+01	2.93E+00	5.36E+00	1.51E-01	1.94E+01	4.75E-01	7.24E-02

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	3.14E+02	2.09E+01	4.24E+00	2.82E-01
% Recovered	9.70E+01	1.01E+02	9.70E+01	1.01E+02
Ether Ext. Balance:	5.45E+01	7.53E+00	7.35E-01	1.02E-01
% Recovered	1.20E+02	1.06E+02	1.20E+02	1.06E+02

Effluent:	E14146-149					
Type:	Eo, 100% ClO2 (lab), pre-O2,30 min				Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	4.74E+02	3.95E+01	6.78E+00	1.91E-01	2.07E+02	6.40E+00	9.15E-02
NVW	4.70E+02	3.92E+01	6.55E+00	1.85E-01	2.12E+02	6.35E+00	8.84E-02
NVEE I	6.16E+01	5.14E+00	1.41E+00	3.97E-02	1.29E+02	8.32E-01	1.90E-02
NVEE II	3.80E+01	3.17E+00	2.65E-01	7.46E-03	4.24E+02	5.13E-01	3.58E-03
NVNEE	3.42E+02	2.85E+01	6.00E+00	1.69E-01	1.69E+02	4.62E+00	8.10E-02
NVEEA	5.31E+01	4.42E+00	1.15E+00	3.24E-02	1.37E+02	7.17E-01	1.55E-02
NVEEP	3.28E+00	2.73E-01	1.60E-01	4.50E-03	6.07E+01	4.42E-02	2.16E-03
NVEEN	1.97E+00	1.65E-01	6.34E-02	1.79E-03	9.21E+01	2.67E-02	8.56E-04
Volatile	4.04E+00	3.37E-01	2.30E-01	6.48E-03	5.20E+01	5.46E-02	3.11E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	4.42E+02	7.67E+00	5.97E+00	1.04E-01
% Recovered	9.41E+01	1.17E+02	9.41E+01	1.17E+02
Ether Ext. Balance:	5.84E+01	1.37E+00	7.88E-01	1.85E-02
% Recovered	9.47E+01	9.74E+01	9.47E+01	9.74E+01

Effluent: DC4146-174
Type: 100% ClO2 (lab), pre-O2 pulp, 1 min

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	2.24E+02	1.86E+01	8.68E+00	2.45E-01	7.62E+01	3.02E+00	1.17E-01
NVW	2.10E+02	1.75E+01	8.12E+00	2.29E-01	7.66E+01	2.84E+00	1.10E-01
NVEE I	2.99E+01	2.49E+00	1.71E+00	4.80E-02	5.19E+01	4.04E-01	2.30E-02
NVEE II	8.58E+00	7.15E-01	1.11E+00	3.13E-02	2.29E+01	1.16E-01	1.50E-02
NVNEE	1.80E+02	1.50E+01	6.58E+00	1.85E-01	8.09E+01	2.43E+00	8.88E-02
NVEEA	1.72E+01	1.43E+00	1.43E+00	4.03E-02	3.55E+01	2.32E-01	1.93E-02
NVEEP	1.58E+00	1.32E-01	1.41E-01	3.99E-03	3.31E+01	2.14E-02	1.91E-03
NVEEN	**********	**********	0.00E+00	0.00E+00	ERR	*********	0.00E+00
Volatile	1.32E+01	1.10E+00	5.60E-01	1.58E-02	6.95E+01	1.78E-01	7.56E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	2.18E+02	9.39E+00	2.95E+00	1.27E-01
% Recovered	1.04E+02	1.16E+02	1.04E+02	1.16E+02
Ether Ext. Balance:	1.79E+01	1.57E+00	2.41E-01	2.12E-02
% Recovered	5.98E+01	9.22E+01	5.98E+01	9.22E+01

Effluent: E14146-175
Type: Eo, 100% ClO2 (lab), pre-O2, 1 min

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	4.86E+02	4.05E+01	5.53E+00	1.56E-01	2.60E+02	6.56E+00	7.47E-02
NVW	4.71E+02	3.93E+01	4.80E+00	1.35E-01	2.90E+02	6.36E+00	6.48E-02
NVEE I	5.31E+01	4.42E+00	7.77E-01	2.19E-02	2.02E+02	7.17E-01	1.05E-02
NVEE II	4.59E+01	3.82E+00	2.33E-01	6.58E-03	5.81E+02	6.19E-01	3.15E-03
NVNEE	3.73E+02	3.11E+01	3.86E+00	1.09E-01	2.85E+02	5.03E+00	5.22E-02
NVEEA	4.63E+01	3.86E+00	6.54E-01	1.84E-02	2.09E+02	6.25E-01	8.83E-03
NVEEP	3.17E+00	2.64E-01	8.97E-02	2.53E-03	1.04E+02	4.28E-02	1.21E-03
NVEEN	4.19E+00	3.49E-01	4.57E-02	1.29E-03	2.71E+02	5.66E-02	6.18E-04
Volatile	1.52E+01	1.27E+00	7.30E-01	2.06E-02	6.16E+01	2.05E-01	9.86E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	4.72E+02	4.88E+00	6.37E+00	6.58E-02
% Recovered	1.00E+02	1.02E+02	1.00E+02	1.02E+02
Ether Ext. Balance:	5.37E+01	7.89E-01	7.24E-01	1.07E-02
% Recovered	1.01E+02	1.02E+02	1.01E+02	1.02E+02

Effluent:	DC4207-25						
Type:	100% ClO2 (lab), pre-O2, 3s					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	1.65E+02	1.37E+01	5.23E+00	1.47E-01	9.34E+01	2.23E+00	7.06E-02
NVW	1.58E+02	1.32E+01	4.58E+00	1.29E-01	1.02E+02	2.14E+00	6.18E-02
NVEE I	1.34E+01	1.12E+00	1.34E+00	3.79E-02	2.95E+01	1.81E-01	1.81E-02
NVEE II	6.79E+00	5.66E-01	4.61E-01	1.30E-02	4.36E+01	9.17E-02	6.22E-03
NVNEE	1.55E+02	1.29E+01	2.93E+00	8.26E-02	1.56E+02	2.09E+00	3.96E-02
NVEEA	1.11E+01	9.25E-01	1.01E+00	2.85E-02	3.25E+01	1.50E-01	1.37E-02
NVEEP	1.59E+00	1.33E-01	1.21E-01	3.41E-03	3.89E+01	2.15E-02	1.63E-03
NVEEN	3.67E+00	3.05E-01	9.70E-02	2.73E-03	1.12E+02	4.95E-02	1.31E-03
Volatile	6.82E+00	5.68E-01	6.52E-01	1.84E-02	3.09E+01	9.20E-02	8.80E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	1.75E+02	4.74E+00	2.36E+00	6.40E-02
% Recovered	1.11E+02	1.04E+02	1.11E+02	1.04E+02
Ether Ext. Balance:	1.64E+01	1.23E+00	2.21E-01	1.66E-02
% Recovered	1.22E+02	9.15E+01	1.22E+02	9.15E+01

Effluent:	E14207-25						
Type:	Eo, 100% ClO2 (lab), pre-O2, 3s					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	4.69E+02	3.91E+01	3.80E+00	1.07E-01	3.65E+02	6.33E+00	5.13E-02
NVW	4.35E+02	3.62E+01	3.42E+00	9.65E-02	3.76E+02	5.87E+00	4.62E-02
NVEE I	5.78E+01	4.81E+00	9.27E-01	2.61E-02	1.84E+02	7.80E-01	1.25E-02
NVEE II	4.38E+01	3.65E+00	1.54E-01	4.32E-03	8.44E+02	5.91E-01	2.07E-03
NVNEE	3.17E+02	2.64E+01	2.25E+00	6.34E-02	4.17E+02	4.28E+00	3.04E-02
NVEEA	5.09E+01	4.25E+00	5.62E-01	1.58E-02	2.68E+02	6.88E-01	7.59E-03
NVEEP	3.76E+00	3.13E-01	7.10E-02	2.00E-03	1.57E+02	5.07E-02	9.58E-04
NVEEN	1.76E+00	1.47E-01	7.37E-02	2.08E-03	7.08E+01	2.38E-02	9.96E-04
Volatile	3.45E+01	2.88E+00	3.76E-01	1.06E-02	2.72E+02	4.66E-01	5.08E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	4.19E+02	3.33E+00	5.65E+00	4.50E-02
% Recovered	9.63E+01	9.73E+01	9.63E+01	9.73E+01
Ether Ext. Balance:	5.65E+01	7.07E-01	7.62E-01	9.55E-03
% Recovered	9.78E+01	7.63E+01	9.78E+01	7.63E+01

Effluent:	DC4207-34						
Type:	100% ClO2 (lab), pre-O2, 5 min					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	2.61E+02	2.18E+01	1.24E+01	3.49E-01	6.23E+01	3.53E+00	1.67E-01
NVW	2.55E+02	2.12E+01	1.32E+01	3.72E-01	5.70E+01	3.44E+00	1.78E-01
NVEE I	2.45E+01	2.04E+00	3.82E+00	1.08E-01	1.90E+01	3.31E-01	5.16E-02
NVEE II	1.35E+01	1.12E+00	1.43E+00	4.02E-02	2.80E+01	1.82E-01	1.93E-02
NVNEE	2.06E+02	1.71E+01	6.25E+00	1.76E-01	9.72E+01	2.78E+00	8.44E-02
NVEEA	2.06E+01	1.71E+00	2.94E+00	8.28E-02	2.07E+01	2.78E-01	3.97E-02
NVEEP	2.67E+00	2.22E-01	2.47E-01	6.97E-03	3.19E+01	3.60E-02	3.34E-03
NVEEN	4.08E+00	3.40E-01	1.96E-01	5.52E-03	6.16E+01	5.51E-02	2.65E-03
Volatile	6.65E+00	5.54E-01	**********	**********	**********	8.98E-02	*********

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	2.44E+02	1.15E+01	3.29E+00	1.55E-01
% Recovered	9.57E+01	8.70E+01	9.57E+01	8.70E+01
Ether Ext. Balance:	2.73E+01	3.38E+00	3.69E-01	4.57E-02
% Recovered	1.12E+02	8.86E+01	1.12E+02	8.86E+01

Effluent:	E14207-34						
Type:	Eo, 100% ClO2 (lab), pre-O2, 5 min					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	5.16E+02	4.30E+01	7.26E+00	2.05E-01	2.10E+02	6.97E+00	9.80E-02
NVW	5.13E+02	4.27E+01	6.48E+00	1.83E-01	2.34E+02	6.92E+00	8.75E-02
NVEE I	6.41E+01	5.34E+00	1.33E+00	3.75E-02	1.42E+02	8.65E-01	1.80E-02
NVEE II	5.79E+01	4.82E+00	2.88E-01	8.13E-03	5.94E+02	7.82E-01	3.89E-03
NVNEE	3.47E+02	2.89E+01	3.93E+00	1.11E-01	2.61E+02	4.69E+00	5.31E-02
NVEEA	5.64E+01	4.70E+00	9.86E-01	2.78E-02	1.69E+02	7.61E-01	1.33E-02
NVEEP	4.39E+00	3.66E-01	1.46E-01	4.10E-03	8.91E+01	5.92E-02	1.97E-03
NVEEN	3.60E+00	3.00E-01	1.25E-01	3.52E-03	8.51E+01	4.86E-02	1.69E-03
Volatile	3.38E+00	2.82E-01	7.80E-01	2.20E-02	1.28E+01	4.57E-02	1.05E-02

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	4.69E+02	5.55E+00	6.34E+00	7.49E-02
% Recovered	9.15E+01	8.57E+01	9.15E+01	8.57E+01
Ether Ext. Balance:	6.44E+01	1.26E+00	8.69E-01	1.70E-02
% Recovered	1.00E+02	9.43E+01	1.00E+02	9.43E+01

Effluent: DC4207-51
Type: 100% ClO2 (lab), pre-O2, 1 min

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	2.23E+02	1.86E+01	8.66E+00	2.44E-01	7.62E+01	3.01E+00	1.17E-01
NVW	2.22E+02	1.85E+01	6.96E+00	1.96E-01	9.42E+01	2.99E+00	9.40E-02
NVEE I	2.09E+01	1.74E+00	1.85E+00	5.23E-02	3.33E+01	2.82E-01	2.50E-02
NVEE II	1.03E+01	8.58E-01	6.61E-01	1.86E-02	4.61E+01	1.39E-01	8.93E-03
NVNEE	1.96E+02	1.63E+01	5.09E+00	1.43E-01	1.14E+02	2.65E+00	6.87E-02
NVEEA	1.89E+01	1.57E+00	1.73E+00	4.86E-02	3.23E+01	2.55E-01	2.33E-02
NVEEP	2.10E+00	1.75E-01	1.89E-01	5.33E-03	3.29E+01	2.84E-02	2.55E-03
NVEEN	3.88E+00	3.24E-01	1.11E-01	3.12E-03	1.04E+02	5.24E-02	1.50E-03
Volatile	1.42E+00	1.19E-01	1.70E+00	4.79E-02	2.48E+00	1.92E-02	2.29E-02

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	2.27E+02	7.60E+00	3.07E+00	1.03E-01
% Recovered	1.03E+02	1.09E+02	1.03E+02	1.09E+02
Ether Ext. Balance:	2.48E+01	2.02E+00	3.35E-01	2.73E-02
% Recovered	1.19E+02	1.09E+02	1.19E+02	1.09E+02

Effluent: E14207-51
Type: Eo, 100% ClO2 (lab), pre-O2, 1 min

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	4.66E+02	3.89E+01	4.55E+00	1.28E-01	3.03E+02	6.30E+00	6.14E-02
NVW	4.68E+02	3.90E+01	3.86E+00	1.09E-01	3.59E+02	6.32E+00	5.21E-02
NVEE I	5.61E+01	4.67E+00	7.99E-01	2.25E-02	2.08E+02	7.57E-01	1.08E-02
NVEE II	5.35E+01	4.46E+00	2.09E-01	5.89E-03	7.57E+02	7.22E-01	2.82E-03
NVNEE	3.49E+02	2.91E+01	3.21E+00	9.04E-02	3.21E+02	4.71E+00	4.33E-02
NVEEA	4.53E+01	3.77E+00	6.66E-01	1.88E-02	2.01E+02	6.11E-01	8.99E-03
NVEEP	3.98E+00	3.31E-01	1.03E-01	2.89E-03	1.15E+02	5.37E-02	1.39E-03
NVEEN	2.19E+00	1.82E-01	6.73E-02	1.89E-03	9.63E+01	2.96E-02	9.08E-04
Volatile	**********	6.90E-01	1.94E-02	**********			9.31E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	4.58E+02	4.22E+00	6.19E+00	5.69E-02
% Recovered	9.79E+01	1.09E+02	9.79E+01	1.09E+02
Ether Ext. Balance:	5.14E+01	8.36E-01	6.94E-01	1.13E-02
% Recovered	9.17E+01	1.05E+02	9.17E+01	1.05E+02

Effluent: DC4207-68
Type: 100% ClO2 (lab), pre-O2, 5 min

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	2.60E+02	2.16E+01	1.44E+01	4.06E-01	5.32E+01	3.50E+00	1.95E-01
NVW	2.44E+02	2.03E+01	1.36E+01	3.82E-01	5.31E+01	3.29E+00	1.83E-01
NVEE I	3.07E+01	2.56E+00	3.45E+00	9.72E-02	2.63E+01	4.14E-01	4.66E-02
NVEE II	1.42E+01	1.18E+00	1.30E+00	3.65E-02	3.23E+01	1.91E-01	1.75E-02
NVNEE	2.14E+02	1.79E+01	6.69E+00	1.88E-01	9.48E+01	2.89E+00	9.03E-02
NVEEA	2.82E+01	2.35E+00	3.19E+00	9.00E-02	2.61E+01	3.81E-01	4.31E-02
NVEEP	1.77E+00	1.48E-01	1.73E-01	4.86E-03	3.04E+01	2.40E-02	2.33E-03
NVEEN	2.50E+00	2.08E-01	1.78E-01	5.01E-03	4.15E+01	3.37E-02	2.40E-03
Volatile	1.60E+01	1.33E+00	8.60E-01	2.42E-02	5.50E+01	2.16E-01	1.16E-02

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	2.59E+02	1.14E+01	3.50E+00	1.54E-01
% Recovered	1.06E+02	8.43E+01	1.06E+02	8.43E+01
Ether Ext. Balance:	3.25E+01	3.54E+00	4.39E-01	4.78E-02
% Recovered	1.06E+02	1.03E+02	1.06E+02	1.03E+02

Effluent: E14207-68
Type: Eo, 100% ClO2 (lab), pre-O2, 5 min

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	5.07E+02	4.23E+01	6.34E+00	1.79E-01	2.37E+02	6.85E+00	8.56E-02
NVW	5.04E+02	4.20E+01	6.34E+00	1.79E-01	2.35E+02	6.80E+00	8.56E-02
NVEE I	6.15E+01	5.12E+00	1.10E+00	3.11E-02	1.65E+02	8.30E-01	1.49E-02
NVEE II	4.40E+01	3.67E+00	2.55E-01	7.17E-03	5.12E+02	5.94E-01	3.44E-03
NVNEE	3.68E+02	3.07E+01	4.46E+00	1.26E-01	2.44E+02	4.97E+00	6.02E-02
NVEEA	5.49E+01	4.58E+00	8.40E-01	2.37E-02	1.93E+02	7.42E-01	1.13E-02
NVEEP	3.82E+00	3.18E-01	1.34E-01	3.77E-03	8.44E+01	5.15E-02	1.81E-03
NVEEN	1.18E+00	9.85E-02	8.49E-02	2.39E-03	4.12E+01	1.60E-02	1.15E-03
Volatile	3.38E+00	2.82E-01	0.00E+00	0.00E+00	ERR	4.56E-02	0.00E+00

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	4.73E+02	5.82E+00	6.39E+00	7.85E-02
% Recovered	9.40E+01	9.17E+01	9.40E+01	9.17E+01
Ether Ext. Balance:	5.99E+01	1.06E+00	8.09E-01	1.43E-02
% Recovered	9.75E+01	9.60E+01	9.75E+01	9.60E+01

Effluent:	DC4207-81						
Type:	100% ClO2 (lab), pre-O2, 3 sec					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	1.88E+02	1.57E+01	4.78E+00	1.35E-01	1.16E+02	2.54E+00	6.45E-02
NVW	1.74E+02	1.45E+01	4.52E+00	1.27E-01	1.14E+02	2.35E+00	6.10E-02
NVEE I	1.81E+01	1.51E+00	1.18E+00	3.33E-02	4.52E+01	2.44E-01	1.60E-02
NVEE II	1.13E+01	9.42E-01	3.03E-01	8.55E-03	1.10E+02	1.53E-01	4.10E-03
NVNEE	1.79E+02	1.49E+01	2.61E+00	7.35E-02	2.03E+02	2.42E+00	3.52E-02
NVEEA	1.62E+01	1.35E+00	8.77E-01	2.47E-02	5.48E+01	2.19E-01	1.18E-02
NVEEP	1.40E+00	1.17E-01	9.58E-02	2.70E-03	4.33E+01	1.89E-02	1.29E-03
NVEEN	2.12E+00	1.76E-01	9.99E-02	2.81E-03	6.27E+01	2.86E-02	1.35E-03
Volatile	1.41E+01	1.17E+00	2.64E-01	7.44E-03	1.58E+02	1.90E-01	3.56E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	2.08E+02	4.10E+00	2.81E+00	5.53E-02
% Recovered	1.20E+02	9.07E+01	1.20E+02	9.07E+01
Ether Ext. Balance:	1.98E+01	1.07E+00	2.67E-01	1.45E-02
% Recovered	1.09E+02	9.07E+01	1.09E+02	9.07E+01

Effluent:	E14207-81						
Type:	Eo, 100% ClO2 (lab), pre-O2, 3 sec					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	4.95E+02	4.13E+01	3.16E+00	8.90E-02	4.63E+02	6.68E+00	4.27E-02
NVW	4.81E+02	4.01E+01	3.01E+00	8.47E-02	4.73E+02	6.49E+00	4.06E-02
NVEE I	5.42E+01	4.52E+00	5.47E-01	1.54E-02	2.93E+02	7.32E-01	7.39E-03
NVEE II	3.90E+01	3.25E+00	1.25E-01	3.51E-03	9.27E+02	5.27E-01	1.68E-03
NVNEE	3.75E+02	3.13E+01	2.44E+00	6.88E-02	4.54E+02	5.06E+00	3.30E-02
NVEEA	4.72E+01	3.93E+00	4.22E-01	1.19E-02	3.31E+02	6.37E-01	5.70E-03
NVEEP	4.37E+00	3.65E-01	7.06E-02	1.99E-03	1.83E+02	5.91E-02	9.53E-04
NVEEN	1.79E+00	1.49E-01	4.55E-02	1.28E-03	1.16E+02	2.41E-02	6.14E-04
Volatile	1.41E+01	1.18E+00	1.52E-01	4.28E-03	2.75E+02	1.91E-01	2.05E-03

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	4.68E+02	3.11E+00	6.32E+00	4.20E-02
% Recovered	9.74E+01	1.04E+02	9.74E+01	1.04E+02
Ether Ext. Balance:	5.34E+01	5.39E-01	7.20E-01	7.27E-03
% Recovered	9.84E+01	9.84E+01	9.84E+01	9.84E+01

Effluent:	DC4207-95						
Type:	100% ClO2 (lab), pre-O2, 30 min					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	3.52E+02	2.93E+01	2.48E+01	6.97E-01	4.21E+01	4.75E+00	3.34E-01
NVW	3.42E+02	2.85E+01	2.49E+01	7.00E-01	4.07E+01	4.61E+00	3.36E-01
NVEE I	4.19E+01	3.49E+00	7.84E+00	2.21E-01	1.58E+01	5.65E-01	1.06E-01
NVEE II	2.49E+01	2.08E+00	3.26E+00	9.19E-02	2.26E+01	3.36E-01	4.40E-02
NVNEE	2.85E+02	2.38E+01	1.15E+01	3.25E-01	7.31E+01	3.85E+00	1.56E-01
NVEEA	3.95E+01	3.29E+00	6.87E+00	1.93E-01	1.70E+01	5.33E-01	9.27E-02
NVEEP	2.54E+00	2.11E-01	2.45E-01	6.91E-03	3.06E+01	3.43E-02	3.31E-03
NVEEN	3.99E+00	3.32E-01	2.09E-01	5.88E-03	5.65E+01	5.38E-02	2.82E-03
Volatile	1.03E+01	8.60E-01	**********	**********	**********	1.39E-01	*********

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	3.52E+02	2.27E+01	4.75E+00	3.06E-01
% Recovered	1.03E+02	9.11E+01	1.03E+02	9.11E+01
Ether Ext. Balance:	4.60E+01	7.32E+00	6.21E-01	9.89E-02
% Recovered	1.10E+02	9.33E+01	1.10E+02	9.33E+01

Effluent:	E14207-95						
Type:	Eo, 100% ClO2 (lab), pre-O2, 30 min					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	4.96E+02	4.13E+01	7.66E+00	2.16E-01	1.92E+02	6.70E+00	1.03E-01
NVW	5.00E+02	4.16E+01	7.65E+00	2.15E-01	1.93E+02	6.75E+00	1.03E-01
NVEE I	9.48E+01	7.90E+00	1.61E+00	4.54E-02	1.74E+02	1.28E+00	2.17E-02
NVEE II	3.93E+01	3.28E+00	2.48E-01	7.00E-03	4.68E+02	5.31E-01	3.35E-03
NVNEE	3.49E+02	2.91E+01	5.45E+00	1.53E-01	1.89E+02	4.71E+00	7.35E-02
NVEEA	8.73E+01	7.27E+00	1.22E+00	3.44E-02	2.12E+02	1.18E+00	1.65E-02
NVEEP	4.61E+00	3.84E-01	1.57E-01	4.44E-03	8.66E+01	6.22E-02	2.13E-03
NVEEN	1.28E+01	1.07E+00	1.00E-01	2.82E-03	3.78E+02	1.73E-01	1.35E-03
Volatile	**********	**********	1.00E-02	2.82E-04	**********	**********	1.35E-04

	(g)	(kg)	(tonne)
Dry Pulp Weight:	3.00E+02	3.00E-01	3.00E-04

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	1.62E+01

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	4.83E+02	7.31E+00	6.52E+00	9.86E-02
% Recovered	9.66E+01	9.55E+01	9.66E+01	9.55E+01
Ether Ext. Balance:	1.05E+02	1.48E+00	1.41E+00	1.99E-02
% Recovered	1.10E+02	9.18E+01	1.10E+02	9.18E+01

Appendix 8B: Model Compound Data

Effluent:	SE4146-186						
Type:	DI water					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	2.50E-02	2.08E-03	0.00E+00	0.00E+00	ERR	ERR	ERR
NVW	1.50E-02	1.25E-03	0.00E+00	0.00E+00	ERR	ERR	ERR
NVEE I	1.19E-02	9.90E-04	0.00E+00	0.00E+00	ERR	ERR	ERR
NVEE II	6.25E-03	5.21E-04	0.00E+00	0.00E+00	ERR	ERR	ERR
NVNEE	7.50E-03	6.25E-04	0.00E+00	0.00E+00	ERR	ERR	ERR
NVEEA	0.00E+00	0.00E+00	0.00E+00	0.00E+00	ERR	ERR	ERR
NVEEP	6.25E-04	5.21E-05	0.00E+00	0.00E+00	ERR	ERR	ERR
NVEEN	4.45E-02	3.71E-03	0.00E+00	0.00E+00	ERR	ERR	ERR
Volatile	1.00E-02	8.33E-04	0.00E+00	0.00E+00	ERR	ERR	ERR

	(g)	(kg)	(tonne)
Dry Pulp Weight:	0.00E+00	0.00E+00	0.00E+00

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	0.00E+00

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	2.56E-02	0.00E+00	ERR	ERR
% Recovered	1.71E+02	ERR	ERR	ERR
Ether Ext. Balance:	4.52E-02	0.00E+00	ERR	ERR
% Recovered	3.80E+02	ERR	ERR	ERR

Effluent:	SE4146-103A						
Type:	2,4,6 trichlorophenol solution					Carbon	Chlorine
Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	(kg/bdtp)	(kg/bdtp)
Whole	0.00E+00	0.00E+00	1.02E+00	2.86E-02	0.00E+00	ERR	ERR
NVW	0.00E+00	0.00E+00	0.00E+00	0.00E+00	ERR	ERR	ERR
NVEE I	0.00E+00	0.00E+00	7.37E-01	2.08E-02	0.00E+00	ERR	ERR
NVEE II	0.00E+00	0.00E+00	0.00E+00	0.00E+00	ERR	ERR	ERR
NVNEE	0.00E+00	0.00E+00	0.00E+00	0.00E+00	ERR	ERR	ERR
NVEEA	0.00E+00	0.00E+00	2.70E-03	7.61E-05	0.00E+00	ERR	ERR
NVEEP	0.00E+00	0.00E+00	1.00E+00	2.82E-02	0.00E+00	ERR	ERR
NVEEN	0.00E+00	0.00E+00	0.00E+00	0.00E+00	ERR	ERR	ERR
Volatile	0.00E+00	0.00E+00	1.02E+00	2.86E-02	0.00E+00	ERR	ERR

	(g)	(kg)	(tonne)
Dry Pulp Weight:	0.00E+00	0.00E+00	0.00E+00

Effluent Volume Extracted (L):	4.00E+00
Total Effluent Volume (L):	0.00E+00

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	0.00E+00	7.37E-01	ERR	ERR
% Recovered	ERR	ERR	ERR	ERR
Ether Ext. Balance:	0.00E+00	1.00E+00	ERR	ERR
% Recovered	ERR	1.36E+02	ERR	ERR

Effluent: SE4146-187
Type: p-Bromophenol

Fraction	mg C	mM C	mg Cl	mM Cl	C/Cl	Carbon (kg/bdtp)	Chlorine (kg/bdtp)
Whole	1.00E+02	8.36E+00	5.35E+01	1.51E+00	5.55E+00	ERR	ERR
NVW	5.95E+01	4.96E+00	3.08E+01	8.68E-01	5.71E+00	ERR	ERR
NVEE I	6.29E+01	5.24E+00	3.25E+01	9.16E-01	5.72E+00	ERR	ERR
NVEE II	6.25E-03	5.21E-04	6.30E-02	1.77E-03	2.93E-01	ERR	ERR
NVNEE	7.50E-03	6.25E-04	7.68E-02	2.16E-03	2.89E-01	ERR	ERR
NVEEA	3.36E-01	2.80E-02	1.61E-02	4.54E-04	6.16E+01	ERR	ERR
NVEEP	4.34E+01	3.62E+00	2.41E+01	6.80E-01	5.32E+00	ERR	ERR
NVEEN	8.07E+00	6.72E-01	2.89E+00	8.13E-02	8.27E+00	ERR	ERR
Volatile	4.08E+01	3.40E+00	2.27E+01	6.38E-01	5.32E+00	ERR	ERR

	(g)	(kg)	(tonne)
Dry Pulp Weight:	0.00E+00	0.00E+00	0.00E+00

Effluent Volume Extracted (L): 4.00E+00
Total Effluent Volume (L): 0.00E+00

	mg C	mg Cl	kg C/bdtp	kg Cl/bdtp
Overall Balance:	6.29E+01	3.27E+01	ERR	ERR
% Recovered	1.06E+02	1.06E+02	ERR	ERR
Ether Ext. Balance:	5.18E+01	2.71E+01	ERR	ERR
% Recovered	8.24E+01	8.32E+01	ERR	ERR

APPENDIX 9: ANALYSIS OF VARIANCE TABLES

Appendix 9A: AOX Method Development

Effect of Shaking Time on Determined Blank AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Shaking Time)	4	0.280	7.009E-02	10.84**
Error	14	9.053E-02	6.446E-03	
Total	18	0.371		

Term	Count	Mean	Standard Error
All	19	1.419	
A (Shaking Time)			
1 hour	4	1.588	4.020E-02
4 hours	4	1.363	4.020E-02
8 hours	4	1.325	4.020E-02
16 hours	4	1.523	4.020E-02
24 hours	3	1.260	4.642E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of Shaking Time on Determined Standard AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Shaking Time)	4	0.209	5.221E-02	1.56
Error	15	0.502	3.349E-02	
Total	19	0.711		

Term	Count	Mean	Standard Error
All	20	19.683	
A (Shaking Time)			
1 hour	4	19.535	9.150E-02
4 hours	4	19.653	9.150E-02
8 hours	4	19.670	9.150E-02
16 hours	4	19.705	9.150E-02
24 hours	3	19.853	9.150E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of Shaking Time on Determined Mill (C+D) Effluent AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Shaking Time)	4	0.165	4.124E-02	0.20
Error	13	2.637	0.203	
Total	17	2.802		

Term	Count	Mean	Standard Error
All	18	7.982	
A (Shaking Time)			
1 hour	4	8.070	0.225
4 hours	4	8.080	0.225
8 hours	4	7.830	0.225
16 hours	3	7.953	0.260
24 hours	3	7.967	0.260

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of Shaking Time on Determined Mill E Effluent AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Shaking Time)	4	1.657	0.414	4.87**
Error	8	0.681	8.511E-02	
Total	12	2.338		

Term	Count	Mean	Standard Error
All	13	17.947	
A (Shaking Time)			
1 hour	3	18.070	0.168
4 hours	3	18.360	0.168
8 hours	2	17.270	0.206
16 hours	2	17.670	0.206
24 hours	3	18.047	0.168

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of Bleaching Sequence on Breakthrough:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	144.637	72.318	8.15**
B(Effluent Rep.)	1	56.699	56.699	6.39**
AB	2	13.180	6.590	0.74
C(Stage)	1	130.681	130.681	14.74**
AC	2	0.896	0.448	0.05
BC	1	21.517	21.517	2.43
ABC	2	17.016	8.508	0.96
Error	21	186.238	8.868	
Total	32	555.786		

Term	Count	Mean	Standard Error
All	33	6.594	
A (Sequence)			
1: D(EO)	11	6.631	0.898
2: OD(EO)	11	8.953	0.898
3: OC(EO)	11	4.197	0.898
B(Effluent Replication)			
1	17	7.605	0.722
2	16	5.519	0.745
C(Stage)			
1: D or C Stage	18	8.482	0.702
2: (EO) Stage	15	4.327	0.769
AB(Seq., Eff. Repl.)			
1,1	6	7.282	1.216
1,2	5	5.850	1.332
2,1	5	11.434	1.332
2,2	6	6.885	1.216
3,1	6	4.738	1.216
3,2	5	3.548	1.332
AC(Seq., Stage)			
1,1	6	8.373	1.216
1,2	5	4.540	1.332
2,1	6	11.343	1.216
2,2	5	6.084	1.332
3,1	6	5.730	1.216
3,2	5	2.358	1.332
BC(Eff. Repl., Stage)			
1,1	9	8.993	0.993

BC(Eff. Repl., Stage)			
1,2	8	6.044	1.053
2,1	9	7.971	0.993
2,2	7	2.366	1.126
ABC			
1,1,1	3	9.133	1.719
1,1,2	3	5.430	1.719
1,2,1	3	7.613	1.719
1,2,2	2	3.205	2.106
2,1,1	3	11.740	1.719
2,1,2	2	10.975	2.106
2,2,1	3	10.947	1.719
2,2,2	3	2.823	1.719
3,1,1	3	6.107	1.719
3,1,2	3	3.370	1.719
3,2,1	3	5.353	1.719
3,2,2	2	0.840	2.106

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of AOX Conditions on Adsorption-1 AOX Using Double Adsorption System:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	2	1.935	0.967	40.38**
Error	6	0.144	2.395E-02	
Total	8	2.079		

Term	Count	Mean	Standard Error
All	9	11.41	
A (Method)			
80 mg C	3	10.897	8.935E-02
120 mg C	3	12.020	8.935E-02
120 mg + extra NO_3^-	3	11.313	8.935E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of AOX Conditions on Adsorption-2 AOX Using Double Adsorption System:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	2	2.846E-02	1.423E-02	0.67
Error	6	0.128	2.125E-02	
Total	8	0.156		

Term	Count	Mean	Standard Error
All	9	1.310	
A (Method)			
80 mg C	3	1.247	8.417E-02
120 mg C	3	1.383	8.417E-02
120 mg + extra NO_3^-	3	1.300	8.417E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of AOX Conditions on Total AOX Using Double Adsorption System:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	2	2.433	1.216	22.47**
Error	6	0.325	5.413E-02	
Total	8	2.757		

Term	Count	Mean	Standard Error
All	9	12.720	
A (Method)			
80 mg C	3	12.143	0.134
120 mg C	3	13.403	0.134
120 mg + extra NO_3^-	3	12.613	0.134

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of AOX Conditions on Breakthrough Using Double Adsorption System:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	2	3.266E-03	1.633E-03	0.00
Error	6	5.699	0.950	
Total	8	5.702		

Term	Count	Mean	Standard Error
All	9	10.290	
A (Method)			
80 mg C	3	10.263	0.563
120 mg C	3	10.307	0.563
120 mg + extra NO_3^-	3	10.300	0.563

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of AOX Conditions on Adsorption-1 AOX Using Triple Adsorption System:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	2	1.561	0.780	7.59**
Error	5	0.514	0.103	
Total	7	2.075		

Term	Count	Mean	Standard Error
All	8	12.740	
A (Method)			
80 mg C	3	12.227	0.185
120 mg C	2	12.750	0.227
160 mg C	3	13.247	0.185

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of AOX Conditions on Adsorption-2 AOX Using Triple Adsorption System:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	2	0.223	0.117	1.74
Error	5	0.336	6.718E-02	
Total	7	0.569		

Term	Count	Mean	Standard Error
All	8	1.260	
A (Method)			
80 mg C	3	1.480	0.150
120 mg C	3	1.117	0.150
160 mg C	2	1.145	0.183

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of AOX Conditions on Adsorption-3 AOX Using Triple Adsorption System:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	2	0.170	8.521E-02	1.32
Error	4	0.258	6.446E-02	
Total	6	0.428		

Term	Count	Mean	Standard Error
All	7	0.401	
A (Method)			
80 mg C	2	0.645	0.180
120 mg C	3	0.280	0.147
160 mg C	2	0.340	0.180

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of AOX Conditions on Total AOX Using Triple Adsorption System:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	2	0.151	7.561E-02	0.17
Error	3	1.331	0.444	
Total	5	1.482		

Term	Count	Mean	Standard Error
All	6	14.392	
A (Method)			
80 mg C	2	14.360	0.471
120 mg C	2	14.215	0.471
160 mg C	2	14.600	0.471

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of AOX Conditions on Adsorption-2 Breakthrough Using Triple Adsorption System:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	2	12.111	6.056	1.62
Error	4	14.959	3.740	
Total	6	27.070		

Term	Count	Mean	Standard Error
All	7	9.279	
A (Method)			
80 mg C	3	10.793	1.117
120 mg C	2	8.270	1.367
160 mg C	2	8.015	1.367

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Effect of AOX Conditions on Adsorption-3 Breakthrough Using Triple Adsorption System:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	2	6.588	3.294	0.92
Error	3	10.775	3.592	
Total	5	17.363		

Term	Count	Mean	Standard Error
All	6	2.965	
A (Method)			
80 mg C	2	4.445	1.340
120 mg C	2	2.160	1.340
160 mg C	2	2.290	1.340

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Shaker and Column Method Comparison - Adsorption/Column-1 AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	1	1.009	1.009	24.46**
B(Stage)	1	110.050	110.050	2666.79**
AB	1	1.216	1.216	29.47**
Error	8	0.330	4.126E-02	
Total	11	112.605		

Term	Count	Mean	Standard Error
All	12	8.970	
A (Method)			
1: Batch	6	9.260	8.293E-02
2: Column	6	8.680	8.293E-02
B(Stage)			
1: D Stage	6	11.998	8.293E-02
2: (EO) Stage	6	5.942	8.293E-02
AB(Method, Stage)			
1,1	3	11.970	0.117
1,2	3	6.550	0.117
2,1	3	12.027	0.117
2,2	3	5.333	0.117

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Shaker and Column Method Comparison - Adsorption/Column-2 AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	1	3.931	3.931	81.76**
B(Stage)	1	1.392	1.392	28.95**
AB	1	8.166E-04	8.166E-04	0.02
Error	7	0.337	4.808E-02	
Total	10	6.255		

Term	Count	Mean	Standard Error
All	11	1.303	
A (Method)			
1: Batch	5	0.602	9.806E-02
2: Column	6	1.887	8.952E-02
B(Stage)			
1: D Stage	5	1.764	9.806E-02
2: (EO) Stage	6	0.918	8.952E-02
AB(Method, Stage)			
1,1	2	1.025	0.155
1,2	3	0.320	0.127
2,1	3	2.257	0.127
2,2	3	1.517	0.127

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Shaker and Column Method Comparison - Total AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	1	1.197	1.197	29.22**
B(Stage)	1	122.221	122.221	2983.77**
AB	1	1.173	1.173	28.64**
Error	7	0.287	4.096E-02	
Total	10	132.391		

Term	Count	Mean	Standard Error
All	11	9.985	
A (Method)			
1: Batch	5	9.286	9.051E-02
2: Column	6	10.567	8.262E-02
B(Stage)			
1: D Stage	5	13.750	9.051E-02
2: (EO) Stage	6	6.847	8.262E-02
AB(Method, Stage)			
1,1	2	12.950	0.143
1,2	3	6.843	0.117
2,1	3	14.283	0.117
2,2	3	6.850	0.117

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Shaker and Column Method Comparison - Breakthrough:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Method)	1	441.927	441.927	127.20**
B(Stage)	1	4.717	4.717	1.36
AB	1	66.578	66.578	19.16**
Error	7	24.321	3.474	
Total	10	578.578		

Term	Count	Mean	Standard Error
All	11	12.941	
A (Method)			
1: Batch	5	5.720	0.834
2: Column	6	18.960	0.761
B(Stage)			
1: D Stage	5	12.646	0.834
2: (EO) Stage	6	13.188	0.761
AB(Method, Stage)			
1,1	2	7.920	1.318
1,2	3	4.253	1.076
2,1	3	15.797	1.076
2,2	3	22.123	1.076

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Shaking Time Comparison for Lab Produced Effluents - Adsorption-1 AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Stage)	1	86.564	86.564	3596.86**
B(Shaking Time)	1	0.378	0.378	15.71**
AB	1	6.992E-03	6.992E-03	0.29
Error	8	0.193	2.406E-02	
Total	11	87.142		

Term	Count	Mean	Standard Error
All	12	9.083	
A (Stage)			
1: D Stage	6	11.768	6.333E-02
2: (EO) Stage	6	6.397	6.333E-02
B(Shaking Time)			
1: 1 hour	6	8.905	6.333E-02
2: 2 hours	6	9.260	6.333E-02
AB(Stage, Shaking Time)			
1,1	3	11.567	8.956E-02
1,2	3	11.970	8.956E-02
2,1	3	6.243	8.956E-02
2,2	3	6.550	8.956E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Shaking Time Comparison for Lab Produced Effluents - Adsorption-2 AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Stage)	1	1.878	1.878	61.70**
B(Shaking Time)	1	0.328	0.328	10.78**
AB	1	3.081E-02	3.081E-02	1.01
Error	7	0.213	3.043E-02	
Total	10	2.690		

Term	Count	Mean	Standard Error
All	11	0.817	
A (Stage)			
1: D Stage	5	1.300	7.802E-02
2: (EO) Stage	6	0.415	7.122E-02
B(Shaking Time)			
1: 1 hour	6	1.010	7.122E-02
2: 2 hours	5	0.586	7.802E-02
AB(Stage, Shaking Time)			
1,1	3	1.483	0.101
1,2	2	1.025	0.123
2,1	3	0.537	0.101
2,2	3	0.293	0.101

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Shaking Time Comparison for Lab Produced Effluents - Total AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Stage)	1	102.121	102.121	1495.29**
B(Shaking Time)	1	8.963E-04	8.963E-04	0.01
AB	1	1.778E-02	1.778E-02	0.26
Error	7	0.478	6.829E-02	
Total	10	105.276		

Term	Count	Mean	Standard Error
All	11	9.629	
A (Stage)			
1: D Stage	5	13.010	0.117
2: (EO) Stage	6	6.812	0.107
B(Shaking Time)			
1: 1 hour	6	9.915	0.107
2: 2 hours	5	9.286	0.117
AB(Stage, Shaking Time)			
1,1	3	13.050	0.151
1,2	2	12.950	0.185
2,1	3	6.780	0.151
2,2	3	6.843	0.151

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Shaking Time Comparison for Lab Produced Effluents - Breakthrough:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Stage)	1	35.138	35.138	6.81**
B(Shaking Time)	1	32.854	32.854	6.37**
AB	1	3.585E-03	3.585E-03	0.00
Error	7	36.099	5.157	
Total	10	112.588		

Term	Count	Mean	Standard Error
All	11	7.835	
A (Stage)			
1: D Stage	5	10.004	1.016
2: (EO) Stage	6	6.027	0.927
B(Shaking Time)			
1: 1 hour	6	9.597	0.927
2: 2 hours	5	5.720	1.016
AB(Stage, Shaking Time)			
1,1	3	11.393	1.311
1,2	2	7.920	1.606
2,1	3	7.800	1.311
2,2	3	4.253	1.311

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Comparison of Breakthrough for Different Effluent Fractions:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Fraction)	7	808.119	115.446	4.21**
B(Stage)	1	82.745	82.745	3.01*
AB	7	111.067	15.867	0.58
Error	28	768.709	27.454	
Total	43	1767.217		

Term	Count	Mean	Standard Error
All	44	8.597	
A (Fraction)			
1: Whole	6	9.597	2.139
2: NVW	6	4.843	2.139
3: NVEE I	6	7.102	2.139
4: NVEE II	5	11.372	2.343
5: NVNEE	5	16.070	2.343
6: NVEEA	4	13.410	2.620
7: NVEEP	6	8.030	2.139
8: NVEEN	6	1.663	2.139
B(Stage)			
1: D Stage	23	10.177	1.093
2: (EO) Stage	21	6.866	1.143
AB(Fraction, Stage)			
1,1	3	11.393	3.025
1,2	3	7.800	3.025
2,1	3	6.473	3.025
2,2	3	3.213	3.025
3,1	3	7.307	3.025
3,2	3	6.897	3.025
4,1	3	14.780	3.025
4,2	2	6.260	3.705
5,1	3	15.013	3.025
5,2	2	17.655	3.705
6,1	2	13.850	3.705
6,2	2	12.970	3.705
7,1	3	11.043	3.025
7,2	3	5.017	3.025
8,1	3	2.780	3.025
8,2	3	0.547	3.025

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Appendix 9B: Extractor to Extractor Variation

TOC Content in NVEE I:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	6	0.469	7.822E-02	8.35**
B(Stage)	1	0.707	0.707	75.39**
AB	6	0.229	3.820E-02	4.08*
C(Extractor)	1	7.303E-02	7.303E-02	7.79**
AC	6	6.063E-02	1.010E-02	1.08
BC	1	4.480E-04	4.480E-04	0.05
Error	6	5.623E-02	9.372E-03	
Total	27	1.596		

Term	Count	Mean	Standard Error
All	28	0.561	
A (Sequence)			
1: OD(EO)	4	0.364	4.840E-02
2: D(EO)	4	0.531	4.840E-02
3: OD(EO) pH 4	4	0.578	4.840E-02
4: OD(EO) 1800 seconds	4	0.822	4.840E-02
5: OD(EO) 60 seconds	4	0.540	4.840E-02
6: OD(EO) 3 seconds	4	0.484	4.840E-02
7: OD(EO) 300 seconds	4	0.610	4.840E-02
B(Stage)			
1: D Stage	14	0.403	2.587E-02
2: (EO) Stage	14	0.720	2.587E-02
C(Extractor)			
1: Extractor #1	14	0.612	2.587E-02
2: Extractor #2	14	0.510	2.587E-02
AB(Sequence, Stage)			
1,1	2	0.325	6.845E-02
1,2	2	0.402	6.845E-02
2,1	2	0.460	6.845E-02
2,2	2	0.603	6.845E-02
3,1	2	0.516	6.845E-02
3,2	2	0.640	6.845E-02
4,1	2	0.590	6.845E-02
4,2	2	1.056	6.845E-02
5,1	2	0.343	6.845E-02
5,2	2	0.737	6.845E-02
6,1	2	0.213	6.845E-02

Term	Count	Mean	Standard Error
6,2	2	0.756	6.845E-02
7,1	2	0.373	6.845E-02
7,2	2	0.848	6.845E-02
AC(Sequence, Extractor)			
1,1	2	0.391	6.845E-02
1,2	2	0.337	6.845E-02
2,1	2	0.522	6.845E-02
2,2	2	0.541	6.845E-02
3,1	2	0.696	6.845E-02
3,2	2	0.460	6.845E-02
4,1	2	0.947	6.845E-02
4,2	2	0.699	6.845E-02
5,1	2	0.581	6.845E-02
5,2	2	0.500	6.845E-02
6,1	2	0.512	6.845E-02
6,2	2	0.457	6.845E-02
7,1	2	0.640	6.845E-02
7,2	2	0.581	6.845E-02
BC(Stage, Extractor)			
1,1	7	0.458	3.659E-02
1,2	7	0.347	3.659E-02
2,1	7	0.767	3.659E-02
2,2	7	0.673	3.659E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

TOC Content in NVEE II:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	6	0.596	9.925E-02	6.77**
B(Stage)	1	0.386	0.386	26.37**
AB	6	0.489	8.148E-02	5.56**
C(Extractor)	1	8.470E-05	8.470E-05	0.01
AC	6	4.762E-02	7.936E-03	0.54
BC	1	2.088E-02	2.088E-02	1.43
Error	6	8.791E-02	1.465E-02	
Total	27	1.627		

Term	Count	Mean	Standard Error
All	28	0.455	
A (Sequence)			
1: OD(EO)	4	0.317	6.052E-02
2: D(EO)	4	0.786	6.052E-02
3: OD(EO) pH 4	4	0.494	6.052E-02
4: OD(EO) 1800 seconds	4	0.409	6.052E-02
5: OD(EO) 60 seconds	4	0.399	6.052E-02
6: OD(EO) 3 seconds	4	0.341	6.052E-02
7: OD(EO) 300 seconds	4	0.437	6.052E-02
B(Stage)			
1: D Stage	14	0.337	3.235E-02
2: (EO) Stage	14	0.572	3.235E-02
C(Extractor)			
1: Extractor #1	14	0.453	3.235E-02
2: Extractor #2	14	0.456	3.235E-02
AB(Sequence, Stage)			
1,1	2	0.237	8.559E-02
1,2	2	0.397	8.559E-02
2,1	2	0.774	8.559E-02
2,2	2	0.799	8.559E-02
3,1	2	0.617	8.559E-02
3,2	2	0.370	8.559E-02
4,1	2	0.296	8.559E-02
4,2	2	0.522	8.559E-02
5,1	2	0.128	8.559E-02
5,2	2	0.671	8.559E-02
6,1	2	0.122	8.559E-02
6,2	2	0.559	8.559E-02
7,1	2	0.187	8.559E-02
7,2	2	0.688	8.559E-02

Term	Count	Mean	Standard Error
AC(Sequence, Extractor)			
1,1	2	0.311	8.559E-02
1,2	2	0.324	8.559E-02
2,1	2	0.784	8.559E-02
2,2	2	0.789	8.559E-02
3,1	2	0.405	8.559E-02
3,2	2	0.582	8.559E-02
4,1	2	0.394	8.559E-02
4,2	2	0.425	8.559E-02
5,1	2	0.419	8.559E-02
5,2	2	0.379	8.559E-02
6,1	2	0.372	8.559E-02
6,2	2	0.309	8.559E-02
7,1	2	0.486	8.559E-02
7,2	2	0.388	8.559E-02
BC(Stage, Extractor)			
1,1	7	0.308	4.575E-02
1,2	7	0.366	4.575E-02
2,1	7	0.598	4.575E-02
2,2	7	0.547	4.575E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Total Ether Extractable TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	6	1.185	0.197	6.91**
B(Stage)	1	2.138	2.138	74.82**
AB	6	1.233	0.206	7.19**
C(Extractor)	1	6.811E-02	6.811E-02	2.38
AC	6	3.826E-02	6.376E-03	0.22
BC	1	1.522E-02	1.522E-02	0.53
Error	6	0.171	2.857E-02	
Total	27	4.849		

Term	Count	Mean	Standard Error
All	28	1.016	
A (Sequence)			
1: OD(EO)	4	0.681	8.452E-02
2: D(EO)	4	1.317	8.452E-02
3: OD(EO) pH 4	4	1.071	8.452E-02
4: OD(EO) 1800 seconds	4	1.232	8.452E-02
5: OD(EO) 60 seconds	4	0.939	8.452E-02
6: OD(EO) 3 seconds	4	0.825	8.452E-02
7: OD(EO) 300 seconds	4	1.047	8.452E-02
B(Stage)			
1: D Stage	14	0.740	4.517E-02
2: (EO) Stage	14	1.292	4.517E-02
C(Extractor)			
1: Extractor #1	14	1.065	4.517E-02
2: Extractor #2	14	0.967	4.517E-02
AB(Sequence, Stage)			
1,1	2	0.562	0.120
1,2	2	0.800	0.120
2,1	2	1.234	0.120
2,2	2	1.401	0.120
3,1	2	1.133	0.120
3,2	2	1.010	0.120
4,1	2	0.886	0.120
4,2	2	1.578	0.120
5,1	2	0.470	0.120
5,2	2	1.408	0.120
6,1	2	0.335	0.120
6,2	2	1.315	0.120
7,1	2	0.559	0.120
7,2	2	1.536	0.120

Term	Count	Mean	Standard Error
AC(Sequence, Extractor)			
1,1	2	0.701	0.120
1,2	2	0.660	0.120
2,1	2	1.306	0.120
2,2	2	1.329	0.120
3,1	2	1.101	0.120
3,2	2	1.042	0.120
4,1	2	1.341	0.120
4,2	2	1.123	0.120
5,1	2	0.999	0.120
5,2	2	0.879	0.120
6,1	2	0.884	0.120
6,2	2	0.766	0.120
7,1	2	1.126	0.120
7,2	2	0.969	0.120
BC(Stage, Extractor)			
1,1	7	0.766	6.389E-02
1,2	7	0.714	6.389E-02
2,1	7	1.365	6.389E-02
2,2	7	1.220	6.389E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Appendix 9C: Comparison of OC(EO), OD(EO), and D(EO) Bleaching Sequences

Whole Effluent TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	87.342	43.671	191.15**
B (Stage)	1	80.290	80.290	351.43**
AB	2	23.582	11.791	51.61**
Error	6	1.371	0.228	
Total	11	192.585		

Term	Count	Mean	Standard Error
All	12	8.373	
A (Sequence)			
OC(EO)	4	8.020	0.239
OD(EO)	4	5.260	0.239
D(EO)	4	11.84	0.239
B (Stage)			
D/C	6	5.787	0.195
(EO)	6	10.96	0.195
AB (Sequence, Stage)			
OC(EO), D/C	2	6.255	0.338
OC(EO), (EO)	2	9.785	0.338
OD(EO), D/C	2	3.825	0.338
OD(EO), (EO)	2	6.695	0.338
D(EO), D/C	2	7.28	0.338
D(EO), (EO)	2	16.4	0.338

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Whole Effluent log(C/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	1.358	0.679	2065.41**
B (Stage)	1	1.341	1.341	4079.89**
AB	2	8.156E-03	4.078E-03	12.41**
Error	6	1.972E-03	3.287E-04	
Total	11	2.709		

Term	Count	Mean	Standard Error
All	12	0.332	
A (Sequence)			
OC(EO)	4	0.806	9.065E-03
OD(EO)	4	6.289E-02	9.065E-03
D(EO)	4	0.127	9.065E-03
B (Stage)			
D/C	6	0.666	7.401E-03
(EO)	6	-2.28E-03	7.401E-03
AB (Sequence, Stage)			
OC(EO), D/C	2	1.156	1.282E-02
OC(EO), (EO)	2	0.456	1.282E-02
OD(EO), D/C	2	0.418	1.282E-02
OD(EO), (EO)	2	-0.293	1.282E-02
D(EO), D/C	2	0.424	1.282E-02
D(EO), (EO)	2	-0.171	1.282E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE I % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	85.881	49.940	47.82**
B (Stage)	1	0.114	0.114	0.13
AB	2	11.885	5.943	6.62**
Error	6	5.388	0.898	
Total	11	103.268		

Term	Count	Mean	Standard Error
All	12	7.626	
A (Sequence)			
OC(EO)	4	11.25	0.474
OD(EO)	4	6.763	0.474
D(EO)	4	4.868	0.474
B (Stage)			
D/C	6	7.723	0.387
(EO)	6	7.528	0.387
AB (Sequence, Stage)			
OC(EO), D/C	2	9.945	0.670
OC(EO), (EO)	2	12.55	0.670
OD(EO), D/C	2	7.435	0.670
OD(EO), (EO)	2	6.090	0.670
D(EO), D/C	2	5.790	0.670
D(EO), (EO)	2	3.945	0.670

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE I log(Cl/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	1.150	0.575	148.36**
B (Stage)	1	1.571	1.571	405.45**
AB	2	4.354E-02	2.177E-02	5.62**
Error	6	2.325E-02	3.875E-03	
Total	11	2.788		

Term	Count	Mean	Standard Error
All	12	0.622	
A (Sequence)			
OC(EO)	4	1.058	3.113E-02
OD(EO)	4	0.370	3.113E-02
D(EO)	4	0.438	3.113E-02
B (Stage)			
D/C	6	0.984	2.541E-02
(EO)	6	0.260	2.541E-02
AB (Sequence, Stage)			
OC(EO), D/C	2	1.501	4.401E-02
OC(EO), (EO)	2	0.615	4.401E-02
OD(EO), D/C	2	0.715	4.401E-02
OD(EO), (EO)	2	2.530E-02	4.401E-02
D(EO), D/C	2	0.736	4.401E-02
D(EO), (EO)	2	0.140	4.401E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE II % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	6.256	3.128	0.78
B (Stage)	1	0.143	0.143	0.04
AB	2	31.235	15.618	3.91*
Error	6	23.951	3.992	
Total	11	61.585		

Term	Count	Mean	Standard Error
All	12	6.661	
A (Sequence)			
OC(EO)	4	6.775	0.999
OD(EO)	4	5.725	0.999
D(EO)	4	7.483	0.999
B (Stage)			
D/C	6	6.770	0.816
(EO)	6	6.552	0.816
AB (Sequence, Stage)			
OC(EO), D/C	2	5.135	1.413
OC(EO), (EO)	2	8.415	1.413
OD(EO), D/C	2	5.440	1.413
OD(EO), (EO)	2	6.010	1.413
D(EO), D/C	2	9.735	1.413
D(EO), (EO)	2	5.230	1.413

**Significant at 95% confidence level.

*Significant at 90% confidence level

NVEE II log(Cl/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	0.204	0.102	9.03**
B (Stage)	1	2.741	2.741	242.91**
AB	2	0.328	0.164	14.53**
Error	6	6.771E-02	1.128E-02	
Total	11	3.341		

Term	Count	Mean	Standard Error
All	12	0.223	
A (Sequence)			
OC(EO)	4	0.407	5.311E-02
OD(EO)	4	0.122	5.311E-02
D(EO)	4	0.140	5.311E-02
B (Stage)			
D/C	6	0.701	4.336E-02
(EO)	6	-0.255	4.336E-02
AB (Sequence, Stage)			
OC(EO), D/C	2	0.734	7.511E-02
OC(EO), (EO)	2	7.94E-02	7.511E-02
OD(EO), D/C	2	0.830	7.511E-02
OD(EO), (EO)	2	-0.586	7.511E-02
D(EO), D/C	2	0.538	7.511E-02
D(EO), (EO)	2	-0.259	7.511E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVNEE % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	171.662	85.831	3.17
B (Stage)	1	55.901	55.901	2.06
AB	2	130.562	65.281	2.41
Error	6	162.485	27.081	
Total	11	520.609		

Term	Count	Mean	Standard Error
All	12	78.06	
A (Sequence)			
OC(EO)	4	73.10	2.602
OD(EO)	4	82.27	2.602
D(EO)	4	78.80	2.602
B (Stage)			
D/C	6	75.90	2.124
(EO)	6	80.22	2.124
AB (Sequence, Stage)			
OC(EO), D/C	2	73.95	3.680
OC(EO), (EO)	2	72.25	3.680
OD(EO), D/C	2	81.70	3.680
OD(EO), (EO)	2	82.85	3.680
D(EO), D/C	2	72.05	3.680
D(EO), (EO)	2	85.55	3.680

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVNEE log(Cl/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	1.258	0.629	322.37**
B (Stage)	1	0.698	0.698	357.62**
AB	2	5.581E-03	2.790E-03	1.43
Error	6	1.171E-02	1.951E-03	
Total	11	1.974		

Term	Count	Mean	Standard Error
All	12	0.202	
A (Sequence)			
OC(EO)	4	0.653	2.209E-02
OD(EO)	4	-9.11E-02	2.209E-02
D(EO)	4	4.374E-02	2.209E-02
B (Stage)			
D/C	6	0.443	1.803E-02
(EO)	6	-3.92E-02	1.803E-02
AB (Sequence, Stage)			
OC(EO), D/C	2	0.915	3.124E-02
OC(EO), (EO)	2	0.392	3.124E-02
OD(EO), D/C	2	0.160	3.124E-02
OD(EO), (EO)	2	-0.342	3.124E-02
D(EO), D/C	2	0.255	3.124E-02
D(EO), (EO)	2	-0.168	3.124E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEA % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	32.545	16.273	37.07**
B (Stage)	1	7.008E-03	7.008E-03	0.02
AB	2	15.537	7.768	17.70**
Error	6	2.634	0.439	
Total	11	50.723		

Term	Count	Mean	Standard Error
All	12	5.954	
A (Sequence)			
OC(EO)	4	8.140	0.331
OD(EO)	4	5.558	0.331
D(EO)	4	4.165	0.331
B (Stage)			
D/C	6	5.978	0.270
(EO)	6	5.930	0.270
AB (Sequence, Stage)			
OC(EO), D/C	2	6.555	0.469
OC(EO), (EO)	2	9.725	0.469
OD(EO), D/C	2	6.385	0.469
OD(EO), (EO)	2	4.730	0.469
D(EO), D/C	2	4.995	0.469
D(EO), (EO)	2	3.335	0.469

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEA log(Cl/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	1.298	0.649	326.31**
B (Stage)	1	1.512	1.512	760.52**
AB	2	4.484E-02	2.242E-02	11.28**
Error	6	1.193E-02	1.988E-03	
Total	11	2.867		

Term	Count	Mean	Standard Error
All	12	0.603	
A (Sequence)			
OC(EO)	4	1.067	2.229E-02
OD(EO)	4	0.342	2.229E-02
D(EO)	4	0.401	2.229E-02
B (Stage)			
D/C	6	0.958	1.820E-02
(EO)	6	0.248	1.820E-02
AB (Sequence, Stage)			
OC(EO), D/C	2	1.479	3.153E-02
OC(EO), (EO)	2	0.655	3.153E-02
OD(EO), D/C	2	0.724	3.153E-02
OD(EO), (EO)	2	-4.13E-02	3.153E-02
D(EO), D/C	2	0.671	3.153E-02
D(EO), (EO)	2	0.130	3.153E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEP % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	0.941	0.471	47.37**
B (Stage)	1	0.150	0.150	15.06**
AB	2	0.432	0.216	21.77**
Error	6	5.960E-02	9.933E-03	
Total	11	1.583		

Term	Count	Mean	Standard Error
All	12	0.752	
A (Sequence)			
OC(EO)	4	1.145	4.983E-02
OD(EO)	4	0.515	4.983E-02
D(EO)	4	0.595	4.983E-02
B (Stage)			
D/C	6	0.863	4.068E-02
(EO)	6	0.640	4.068E-02
AB (Sequence, Stage)			
OC(EO), D/C	2	1.525	7.047E-02
OC(EO), (EO)	2	0.765	7.047E-02
OD(EO), D/C	2	0.500	7.047E-02
OD(EO), (EO)	2	0.530	7.047E-02
D(EO), D/C	2	0.565	7.047E-02
D(EO), (EO)	2	0.625	7.047E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEP log(Cl/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	1.037	0.519	54.47**
B (Stage)	1	0.447	0.447	46.93**
AB	2	9.716E-02	4.858E-02	5.10*
Error	6	5.711E-02	9.518E-03	
Total	11	1.638		

Term	Count	Mean	Standard Error
All	12	0.691	
A (Sequence)			
OC(EO)	4	1.101	4.878E-02
OD(EO)	4	0.425	4.878E-02
D(EO)	4	0.548	4.878E-02
B (Stage)			
D/C	6	0.884	3.983E-03
(EO)	6	0.498	3.983E-03
AB (Sequence, Stage)			
OC(EO), D/C	2	1.421	6.898E-02
OC(EO), (EO)	2	0.781	6.898E-02
OD(EO), D/C	2	0.547	6.898E-02
OD(EO), (EO)	2	0.303	6.898E-02
D(EO), D/C	2	0.685	6.898E-02
D(EO), (EO)	2	0.411	6.898E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEP log(Cl/C_{100}):

(Only OD(EO) and D(EO) data used in analysis)

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	1	3.008E-02	3.008E-02	11.88**
B (Stage)	1	0.134	0.134	52.97**
AB	1	4.730E-04	4.730E-04	0.19
Error	4	1.013E-02	2.531E-03	
Total	7	0.175		

Term	Count	Mean	Standard Error
All	8	0.487	
A (Sequence)			
OD(EO)	4	0.425	2.515E-02
D(EO)	4	0.548	2.515E-02
B (Stage)			
D/C	4	0.616	2.515E-02
(EO)	4	0.357	2.515E-02
AB (Sequence, Stage)			
OD(EO), D/C	2	0.547	3.557E-02
OD(EO), (EO)	2	0.303	3.557E-02
D(EO), D/C	2	0.685	3.557E-02
D(EO), (EO)	2	0.411	3.557E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEN % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	0.149	7.440E-02	1.89
B (Stage)	1	0.163	0.163	4.15*
AB	2	4.701E-02	2.350E-02	0.60
Error	6	0.236	3.935E-02	
Total	11	0.595		

Term	Count	Mean	Standard Error
All	12	0.803	
A (Sequence)			
OC(EO)	4	0.685	9.918E-02
OD(EO)	4	0.953	9.918E-02
D(EO)	4	0.773	9.918E-02
B (Stage)			
D/C	6	0.920	8.098E-02
(EO)	6	0.687	8.098E-02
AB (Sequence, Stage)			
OC(EO), D/C	2	0.740	0.140
OC(EO), (EO)	2	0.630	0.140
OD(EO), D/C	2	1.155	0.140
OD(EO), (EO)	2	0.750	0.140
D(EO), D/C	2	0.865	0.140
D(EO), (EO)	2	0.680	0.140

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEN $\log(Cl/C_{100})$:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	0.693	0.347	25.90**
B (Stage)	1	8.715E-02	8.715E-02	6.51**
AB	2	1.055E-03	5.278E-04	0.04
Error	6	8.031E-02	1.338E-02	
Total	11	0.862		

Term	Count	Mean	Standard Error
All	12	0.196	
A (Sequence)			
OC(EO)	4	0.496	5.785E-02
OD(EO)	4	-9.24E-02	5.785E-02
D(EO)	4	0.185	5.785E-02
B (Stage)			
D/C	6	0.281	4.723E-02
(EO)	6	0.111	4.723E-02
AB (Sequence, Stage)			
OC(EO), D/C	2	0.579	8.181E-02
OC(EO), (EO)	2	0.413	8.181E-02
OD(EO), D/C	2	5.277E-03	8.181E-02
OD(EO), (EO)	2	-0.190	8.181E-02
D(EO), D/C	2	0.260	8.181E-02
D(EO), (EO)	2	0.110	8.181E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Volatile % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	20.996	10.498	1.61
B (Stage)	1	75.300	75.300	11.58**
AB	2	7.411	3.705	0.57
Error	6	39.009	6.502	
Total	11	142.716		

Term	Count	Mean	Standard Error
All	12	8.423	
A (Sequence)			
OC(EO)	4	10.188	1.275
OD(EO)	4	7.003	1.275
D(EO)	4	8.080	1.275
B (Stage)			
D/C	6	10.93	1.041
(EO)	6	5.918	1.041
AB (Sequence, Stage)			
OC(EO), D/C	2	12.19	1.803
OC(EO), (EO)	2	8.190	1.803
OD(EO), D/C	2	8.905	1.803
OD(EO), (EO)	2	5.100	1.803
D(EO), D/C	2	11.70	1.803
D(EO), (EO)	2	4.465	1.803

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Volatile log(Cl/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	1.131	0.565	2.85
B (Stage)	1	1.444	1.444	7.28**
AB	2	2.784E-02	1.392E-02	0.07
Error	6	1.190	0.198	
Total	11	3.793		

Term	Count	Mean	Standard Error
All	12	0.131	
A (Sequence)			
OC(EO)	4	0.543	0.223
OD(EO)	4	4.469E-02	0.223
D(EO)	4	-0.194	0.223
B (Stage)			
D/C	6	0.478	0.182
(EO)	6	-0.216	0.182
AB (Sequence, Stage)			
OC(EO), D/C	2	0.957	0.315
OC(EO), (EO)	2	0.129	0.315
OD(EO), D/C	2	0.370	0.315
OD(EO), (EO)	2	-0.281	0.315
D(EO), D/C	2	0.108	0.315
D(EO), (EO)	2	-0.496	0.315

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Appendix 9D: Comparison of pH 2 and pH 4 D Stages in the OD(EO) Bleaching Sequence

Whole Effluent TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	1.163	1.163	31.06**
B (Stage)	1	9.570	9.570	255.63**
AB	1	0.932	0.932	24.88**
Error	4	0.150	3.743E-02	
Total	7	11.814		

Term	Count	Mean	Standard Error
All	8	5.641	
A (pH)			
pH 2	4	5.260	9.674E-02
pH 4	4	6.023	9.674E-02
B (Stage)			
D	4	4.548	9.674E-02
(EO)	4	6.735	9.674E-02
AB (pH, Stage)			
pH 2, D	2	3.825	0.137
pH 2, (EO)	2	6.695	0.137
pH 4, D	2	5.270	0.137
pH 4, (EO)	2	6.775	0.137

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Whole Effluent log(Cl/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	2.217E-03	2.217E-03	12.62**
B (Stage)	1	1.022	1.022	5820.52**
AB	1	8.891E-05	8.891E-05	0.51
Error	4	7.025E-04	1.756E-04	
Total	7	1.025		

Term	Count	Mean	Standard Error
All	8	4.752E-02	
A (pH)			
pH 2	4	6.416E-02	6.626E-03
pH 4	4	3.087E-02	6.626E-03
B (Stage)			
D	4	0.405	6.626E-03
(EO)	4	-0.310	6.626E-03
AB (pH, Stage)			
pH 2, D	2	0.418	9.370E-03
pH 2, (EO)	2	-0.290	9.370E-03
pH 4, D	2	0.392	9.370E-03
pH 4, (EO)	2	-0.330	9.370E-03

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE I % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	7.527	7.527	1.30
B (Stage)	1	0.966	0.966	0.17
AB	1	0.966	0.966	0.17
Error	4	23.225	5.806	
Total	7	32.684		

Term	Count	Mean	Standard Error
All	8	7.755	
A (pH)			
pH 2	4	6.785	1.205
pH 4	4	8.725	1.205
B (Stage)			
D	4	8.103	1.205
(EO)	4	7.408	1.205
AB (pH, Stage)			
pH 2, D	2	7.480	1.704
pH 2, (EO)	2	6.090	1.704
pH 4, D	2	8.725	1.704
pH 4, (EO)	2	8.725	1.704

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE I $\log(Cl/C_{100})$:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	2.332E-02	2.332E-02	8.24**
B (Stage)	1	0.970	0.970	342.65**
AB	1	1.069E-04	1.069E-04	0.04
Error	4	1.132E-02	2.831E-03	
Total	7	1.005		

Term	Count	Mean	Standard Error
All	8	0.316	
A (pH)			
pH 2	4	0.370	2.661E-02
pH 4	4	0.262	2.661E-02
B (Stage)			
D	4	0.664	2.661E-02
(EO)	4	-3.23E-02	2.661E-02
AB (pH, Stage)			
pH 2, D	2	0.715	3.762E-02
pH 2, (EO)	2	2.530E-02	3.762E-02
pH 4, D	2	0.614	3.762E-02
pH 4, (EO)	2	-9.00E-02	3.762E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE I % of total TOC:

(Analysis does not include calculated data)

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	18.252	18.252	8.18*
B (Stage)	1	7.276	7.276	3.26
AB	1	0.882	0.882	0.40
Error	3	6.693	2.231	
Total	6	28.536		

Term	Count	Mean	Standard Error
All	7	8.474	
A (pH)			
pH 2	4	6.785	0.747
pH 4	3	10.16	0.862
B (Stage)			
D	3	9.540	0.862
(EO)	4	7.408	0.747
AB (pH, Stage)			
pH 2, D	2	7.480	1.056
pH 2, (EO)	2	6.090	1.056
pH 4, D	1	11.60	1.494
pH 4, (EO)	2	8.725	1.056

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE I $\log(C_l/C_{100})$:

(Analysis does not include calculated data)

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	1.939E-02	1.939E-02	5.15*
B (Stage)	1	0.772	0.772	204.99**
AB	1	4.318E-05	4.318E-05	0.01
Error	3	1.129E-02	3.763E-03	
Total	6	0.901		

Term	Count	Mean	Standard Error
All	7	0.315	
A (pH)			
pH 2	4	0.370	3.067E-02
pH 4	3	0.260	3.541E-02
B (Stage)			
D	3	0.662	3.541E-02
(EO)	4	-3.23E-02	3.067E-02
AB (pH, Stage)			
pH 2, D	2	0.715	4.338E-02
pH 2, (EO)	2	2.530E-02	4.338E-02
pH 4, D	1	0.610	6.135E-02
pH 4, (EO)	2	-9.00E-02	4.338E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE II % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	6.038	6.038	1.35
B (Stage)	1	9.053	9.053	2.02
AB	1	14.553	14.553	3.25
Error	4	17.909	4.477	
Total	7	47.553		

Term	Count	Mean	Standard Error
All	8	6.594	
A (pH)			
pH 2	4	5.725	1.058
pH 4	4	7.463	1.058
B (Stage)			
D	4	7.658	1.058
(EO)	4	5.530	1.058
AB (pH, Stage)			
pH 2, D	2	5.440	1.496
pH 2, (EO)	2	6.010	1.496
pH 4, D	2	9.875	1.496
pH 4, (EO)	2	5.050	1.496

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE II log(C_l/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	0.127	0.127	3.28
B (Stage)	1	2.980	2.980	76.83**
AB	1	7.535E-02	7.535E-02	1.94
Error	4	0.155	3.878E-02	
Total	7	3.337		

Term	Count	Mean	Standard Error
All	8	-3.43E-03	
A (pH)			
pH 2	4	0.123	9.846E-02
pH 4	4	-0.129	9.846E-02
B (Stage)			
D	4	0.607	9.846E-02
(EO)	4	-0.614	9.846E-02
AB (pH, Stage)			
pH 2, D	2	0.830	0.139
pH 2, (EO)	2	-0.545	0.139
pH 4, D	2	0.384	0.139
pH 4, (EO)	2	-0.643	0.139

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVNEE % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	32.805	32.805	2.52
B (Stage)	1	39.605	39.605	3.04
AB	1	21.780	21.780	1.67
Error	4	52.150	13.038	
Total	7	146.34		

Term	Count	Mean	Standard Error
All	8	80.25	
A (pH)			
pH 2	4	82.27	1.805
pH 4	4	78.23	1.805
B (Stage)			
D	4	78.02	1.805
(EO)	4	82.48	1.805
AB (pH, Stage)			
pH 2, D	2	81.70	2.553
pH 2, (EO)	2	82.85	2.553
pH 4, D	2	74.35	2.553
pH 4, (EO)	2	82.10	2.553

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVNEE $\log(Cl/C_{100})$:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	6.052E-03	6.052E-03	4.33
B (Stage)	1	0.543	0.543	388.13**
AB	1	7.054E-04	7.054E-04	0.50
Error	4	5.596E-03	1.399E-03	
Total	7	0.555		

Term	Count	Mean	Standard Error
All	8	-0.119	
A (pH)			
pH 2	4	-9.13E-02	1.870E-02
pH 4	4	-0.146	1.870E-02
B (Stage)			
D	4	0.142	1.870E-02
(EO)	4	-0.379	1.870E-02
AB (pH, Stage)			
pH 2, D	2	0.160	2.645E-02
pH 2, (EO)	2	-0.343	2.645E-02
pH 4, D	2	0.124	2.645E-02
pH 4, (EO)	2	-0.416	2.645E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEA % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	0.769	0.769	0.31
B (Stage)	1	1.186	1.186	0.47
AB	1	1.566	1.566	0.63
Error	4	10.020	2.505	
Total	7	13.541		

Term	Count	Mean	Standard Error
All	8	5.868	
A (pH)			
pH 2	4	5.558	0.791
pH 4	4	6.178	0.791
B (Stage)			
D	4	6.253	0.791
(EO)	4	5.483	0.791
AB (pH, Stage)			
pH 2, D	2	6.385	1.119
pH 2, (EO)	2	4.730	1.119
pH 4, D	2	6.120	1.119
pH 4, (EO)	2	6.235	1.119

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEA $\log(Cl/C_{100})$:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	6.933E-03	6.933E-03	1.14
B (Stage)	1	1.106	1.106	181.89**
AB	1	9.396E-04	9.396E-04	0.15
Error	4	2.432E-02	6.082E-03	
Total	7	1.139		

Term	Count	Mean	Standard Error
All	8	0.312	
A (pH)			
pH 2	4	0.342	3.899E-02
pH 4	4	0.283	3.899E-02
B (Stage)			
D	4	0.684	3.899E-02
(EO)	4	-5.95E-02	3.899E-02
AB (pH, Stage)			
pH 2, D	2	0.724	5.514E-02
pH 2, (EO)	2	-4.09E-02	5.514E-02
pH 4, D	2	0.644	5.514E-02
pH 4, (EO)	2	-7.81E-02	5.514E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEP % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	3.125E-02	3.125E-02	13.68**
B (Stage)	1	1.036E-02	1.036E-02	4.54*
AB	1	3.362E-03	3.362E-03	1.47
Error	4	9.137E-03	2.284E-03	
Total	7	5.412E-02		

Term	Count	Mean	Standard Error
All	8	0.580	
A (pH)			
pH 2	4	0.518	2.389E-02
pH 4	4	0.643	2.389E-02
B (Stage)			
D	4	0.544	2.389E-02
(EO)	4	0.616	2.389E-02
AB (pH, Stage)			
pH 2, D	2	0.502	3.379E-02
pH 2, (EO)	2	0.533	3.379E-02
pH 4, D	2	0.586	3.379E-02
pH 4, (EO)	2	0.699	3.379E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEP $\log(Cl/C_{100})$:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	6.194E-02	6.194E-02	14.02**
B (Stage)	1	0.132	0.132	29.93**
AB	1	3.684E-04	3.684E-04	0.08
Error	4	1.767E-02	4.419E-03	
Total	7	0.212		

Term	Count	Mean	Standard Error
All	8	0.337	
A (pH)			
pH 2	4	0.425	3.324E-02
pH 4	4	0.249	3.324E-02
B (Stage)			
D	4	0.466	3.324E-02
(EO)	4	0.209	3.324E-02
AB (pH, Stage)			
pH 2, D	2	0.547	4.700E-02
pH 2, (EO)	2	0.303	4.700E-02
pH 4, D	2	0.385	4.700E-02
pH 4, (EO)	2	0.114	4.700E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEN % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	0.383	0.383	0.46
B (Stage)	1	1.130	1.130	1.36
AB	1	0.239	0.239	0.29
Error	4	3.318	0.830	
Total	7	5.070		

Term	Count	Mean	Standard Error
All	8	1.171	
A (pH)			
pH 2	4	0.952	0.455
pH 4	4	1.390	0.455
B (Stage)			
D	4	1.547	0.455
(EO)	4	0.795	0.455
AB (pH, Stage)			
pH 2, D	2	1.155	0.644
pH 2, (EO)	2	0.750	0.644
pH 4, D	2	1.939	0.644
pH 4, (EO)	2	0.841	0.644

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEN log(Cl/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	2.909E-02	2.909E-02	0.71
B (Stage)	1	3.752E-02	3.752E-03	0.92
AB	1	6.402E-03	6.402E-03	0.16
Error	4	0.163	4.087E-02	
Total	7	0.237		

Term	Count	Mean	Standard Error
All	8	-3.05E-02	
A (pH)			
pH 2	4	-9.08E-02	0.101
pH 4	4	2.980E-02	0.101
B (Stage)			
D	4	3.798E-02	0.101
(EO)	4	-9.89E-02	0.101
AB (pH, Stage)			
pH 2, D	2	5.969E-03	0.143
pH 2, (EO)	2	-0.188	0.143
pH 4, D	2	7.000E-02	0.143
pH 4, (EO)	2	-1.03E-02	0.143

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Volatile % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	1.786	1.786	0.66
B (Stage)	1	16.994	16.994	6.30*
AB	1	1.584	1.584	0.59
Error	4	10.799	2.700	
Total	7	31.163		

Term	Count	Mean	Standard Error
All	8	6.53	
A (pH)			
pH 2	4	7.003	0.822
pH 4	4	6.058	0.822
B (Stage)			
D	4	7.988	0.822
(EO)	4	5.073	0.822
AB (pH, Stage)			
pH 2, D	2	8.905	1.162
pH 2, (EO)	2	5.100	1.162
pH 4, D	2	7.070	1.162
pH 4, (EO)	2	5.045	1.162

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Volatile log(Cl/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (pH)	1	0.111	0.111	1.48
B (Stage)	1	1.104	1.104	14.62**
AB	1	1.693E-02	1.693E-02	0.22
Error	4	0.302	7.547E-02	
Total	7	1.534		

Term	Count	Mean	Standard Error
All	8	0.163	
A (pH)			
pH 2	4	4.469E-02	0.137
pH 4	4	0.281	0.137
B (Stage)			
D	4	0.534	0.137
(EO)	4	-0.209	0.137
AB (pH, Stage)			
pH 2, D	2	0.370	0.194
pH 2, (EO)	2	-0.281	0.194
pH 4, D	2	0.698	0.194
pH 4, (EO)	2	-0.137	0.194

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Appendix 9E: Comparison of D Stage Reaction Time in the OD(EO) Bleaching Sequence

Whole Effluent TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	3.540	1.180	47.01**
B (Stage)	1	40.196	40.196	1601.42**
AB	3	3.030	1.010	40.23**
Error	8	0.201	2.509E-02	
Total	15	46.966		

Term	Count	Mean	Standard Error
All	16	5.014	
A (Time)			
3 sec.	4	4.445	7.921E-02
60 sec.	4	4.723	7.921E-02
300 sec.	4	5.213	7.921E-02
1800 sec.	4	5.675	7.921E-02
B (Stage)			
D	8	3.429	5.601E-02
(EO)	8	6.599	5.601E-02
AB (Time, Stage)			
3 sec., D	2	2.385	0.112
3 sec., (EO)	2	6.505	0.112
60 sec., D	2	3.015	0.112
60 sec., (EO)	2	6.430	0.112
300 sec., D	2	3.515	0.112
300 sec., (EO)	2	6.910	0.112
1800 sec., D	2	4.800	0.112
1800 sec., (EO)	2	6.550	0.112

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Whole Effluent log(C/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	0.284	9.459E-02	46.54**
B (Stage)	1	1.481	1.481	728.69**
AB	3	7.998E-03	2.666E-03	1.31
Error	8	1.626E-02	2.032E-03	
Total	15	1.789		

Term	Count	Mean	Standard Error
All	16	-0.123	
A (Time)			
3 sec.	4	-0.316	2.254E-02
60 sec.	4	-0.165	2.254E-02
300 sec.	4	-5.40E-02	2.254E-02
1800 sec.	4	4.207E-02	2.254E-02
B (Stage)			
D	8	0.181	1.593E-02
(EO)	8	-0.428	1.593E-02
AB (Time, Stage)			
3 sec., D	2	-1.75E-02	3.187E-02
3 sec., (EO)	2	-0.614	3.187E-02
60 sec., D	2	0.117	3.187E-02
60 sec., (EO)	2	-0.448	3.187E-02
300 sec., D	2	0.240	3.187E-02
300 sec., (EO)	2	-0.349	3.187E-02
1800 sec., D	2	0.384	3.187E-02
1800 sec., (EO)	2	-0.300	3.187E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE I % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	43.084	14.361	4.09**
B (Stage)	1	38.626	38.626	11.00**
AB	3	9.794	3.265	0.93
Error	8	28.095	3.512	
Total	15	119.599		

Term	Count	Mean	Standard Error
All	16	11.85	
A (Time)			
3 sec.	4	9.860	0.937
60 sec.	4	11.30	0.937
300 sec.	4	11.83	0.937
1800 sec.	4	14.4	0.937
B (Stage)			
D	8	10.29	0.663
(EO)	8	13.40	0.663
AB (Time, Stage)			
3 sec., D	2	7.720	1.325
3 sec., (EO)	2	12.00	1.325
60 sec., D	2	10.94	1.325
60 sec., (EO)	2	11.65	1.325
300 sec., D	2	10.46	1.325
300 sec., (EO)	2	13.20	1.325
1800 sec., D	2	12.05	1.325
1800 sec., (EO)	2	16.75	1.325

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE I % of total AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	198.315	66.105	4.33**
B (Stage)	1	270.602	270.602	17.74**
AB	3	68.963	22.988	1.51
Error	8	122.06	15.258	
Total	15	659.940		

Term	Count	Mean	Standard Error
All	16	22.70	
A (Time)			
3 sec.	4	24.15	1.953
60 sec.	4	16.70	1.953
300 sec.	4	25.73	1.953
1800 sec.	4	24.23	1.953
B (Stage)			
D	8	26.81	1.381
(EO)	8	18.59	1.381
AB (Time, Stage)			
3 sec., D	2	26.65	2.762
3 sec., (EO)	2	21.65	2.762
60 sec., D	2	18.40	2.762
60 sec., (EO)	2	15.00	2.762
300 sec., D	2	31.25	2.762
300 sec., (EO)	2	20.20	2.762
1800 sec., D	2	30.95	2.762
1800 sec., (EO)	2	17.50	2.762

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE I log(C_l/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	0.214	7.146E-02	7.16**
B (Stage)	1	2.671	2.671	267.68**
AB	3	3.023E-02	1.007E-02	1.01
Error	8	7.982E-02	9.977E-03	
Total	15	2.995		

Term	Count	Mean	Standard Error
All	16	0.149	
A (Time)			
3 sec.	4	3.553E-02	4.994E-02
60 sec.	4	3.485E-02	4.994E-02
300 sec.	4	0.233	4.994E-02
1800 sec.	4	0.293	4.994E-02
B (Stage)			
D	8	0.558	3.531E-02
(EO)	8	-0.260	3.531E-02
AB (Time, Stage)			
3 sec., D	2	0.437	7.063E-02
3 sec., (EO)	2	-0.366	7.063E-02
60 sec., D	2	0.381	7.063E-02
60 sec., (EO)	2	-0.312	7.063E-02
300 sec., D	2	0.650	7.063E-02
300 sec., (EO)	2	-0.185	7.063E-02
1800 sec., D	2	0.761	7.063E-02
1800 sec., (EO)	2	-0.176	7.063E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE II % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	3.691	1.230	0.91
B (Stage)	1	88.501	88.501	65.62**
AB	3	9.669	3.223	2.39
Error	8	10.790	1.349	
Total	15	112.651		

Term	Count	Mean	Standard Error
All	16	7.292	
A (Time)			
3 sec.	4	6.640	0.581
60 sec.	4	7.338	0.581
300 sec.	4	7.990	0.581
1800 sec.	4	7.200	0.581
B (Stage)			
D	8	4.940	0.411
(EO)	8	9.643	0.411
AB (Time, Stage)			
3 sec., D	2	4.395	0.821
3 sec., (EO)	2	8.885	0.821
60 sec., D	2	4.070	0.821
60 sec., (EO)	2	10.61	0.821
300 sec., D	2	5.255	0.821
300 sec., (EO)	2	10.73	0.821
1800 sec., D	2	6.040	0.821
1800 sec., (EO)	2	8.360	0.821

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEE II log(Cl/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	0.346	0.115	6.58**
B (Stage)	1	6.249	6.249	356.69**
AB	3	2.910E-02	9.702E-03	0.55
Error	8	0.140	1.751E-02	
Total	15	6.764		

Term	Count	Mean	Standard Error
All	16	-0.165	
A (Time)			
3 sec.	4	-0.394	6.618E-02
60 sec.	4	-0.167	6.618E-02
300 sec.	4	-0.110	6.618E-02
1800 sec.	4	1.083E-02	6.618E-02
B (Stage)			
D	8	0.460	4.679E-02
(EO)	8	-0.790	4.679E-02
AB (Time, Stage)			
3 sec., D	2	0.159	9.359E-02
3 sec., (EO)	2	-0.947	9.359E-02
60 sec., D	2	0.488	9.359E-02
60 sec., (EO)	2	-0.822	9.359E-02
300 sec., D	2	0.522	9.359E-02
300 sec., (EO)	2	-0.742	9.359E-02
1800 sec., D	2	0.670	9.359E-02
1800 sec., (EO)	2	-0.648	9.359E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVNEE % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	51.048	17.016	1.00
B (Stage)	1	68.890	68.890	4.03*
AB	3	48.400	16.133	0.94
Error	8	136.660	17.083	
Total	15	304.998		

Term	Count	Mean	Standard Error
All	16	77.24	
A (Time)			
3 sec.	4	78.23	2.067
60 sec.	4	78.83	2.067
300 sec.	4	77.68	2.067
1800 sec.	4	74.23	2.067
B (Stage)			
D	8	79.31	1.461
(EO)	8	75.16	1.461
AB (Time, Stage)			
3 sec., D	2	82.60	2.923
3 sec., (EO)	2	73.85	2.923
60 sec., D	2	81.00	2.923
60 sec., (EO)	2	76.65	2.923
300 sec., D	2	79.95	2.923
300 sec., (EO)	2	75.40	2.923
1800 sec., D	2	73.70	2.923
1800 sec., (EO)	2	74.75	2.923

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVNEE log(C_l/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	0.322	0.107	38.57**
B (Stage)	1	0.735	0.735	263.93**
AB	3	6.983E-03	2.327E-03	0.84
Error	8	2.227E-02	2.784E-03	
Total	15	1.086		

Term	Count	Mean	Standard Error
All	16	-0.229	
A (Time)			
3 sec.	4	-0.444	2.638E-02
60 sec.	4	-0.231	2.638E-02
300 sec.	4	-0.192	2.638E-02
1800 sec.	4	-4.79E-02	2.638E-02
B (Stage)			
D	8	-1.46E-02	1.865E-02
(EO)	8	-0.443	1.865E-02
AB (Time, Stage)			
3 sec., D	2	-0.250	3.731E-02
3 sec., (EO)	2	-0.639	3.731E-02
60 sec., D	2	1.821E-02	3.731E-02
60 sec., (EO)	2	-0.480	3.731E-02
300 sec., D	2	1.701E-02	3.731E-02
300 sec., (EO)	2	-0.402	3.731E-02
1800 sec., D	2	0.156	3.731E-02
1800 sec., (EO)	2	-0.252	3.731E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEA % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	51.626	17.209	6.08**
B (Stage)	1	37.946	37.946	13.41**
AB	3	2.942	0.981	0.35
Error	8	22.635	2.829	
Total	15	115.148		

Term	Count	Mean	Standard Error
All	16	10.22	
A (Time)			
3 sec.	4	8.588	0.841
60 sec.	4	8.750	0.841
300 sec.	4	10.49	0.841
1800 sec.	4	13.05	0.841
B (Stage)			
D	8	8.679	0.595
(EO)	8	11.76	0.595
AB (Time, Stage)			
3 sec., D	2	6.675	1.189
3 sec., (EO)	2	10.50	1.189
60 sec., D	2	7.765	1.189
60 sec., (EO)	2	9.735	1.189
300 sec., D	2	9.225	1.189
300 sec., (EO)	2	11.75	1.189
1800 sec., D	2	11.05	1.189
1800 sec., (EO)	2	15.05	1.189

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEA % of total AOX:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	120.672	40.224	11.77**
B (Stage)	1	308.881	308.881	90.40**
AB	3	79.402	26.467	7.75**
Error	8	27.335	3.417	
Total	15	536.289		

Term	Count	Mean	Standard Error
All	16	18.39	
A (Time)			
3 sec.	4	17.23	0.924
60 sec.	4	14.45	0.924
300 sec.	4	20.65	0.924
1800 sec.	4	21.25	0.924
B (Stage)			
D	8	22.79	0.654
(EO)	8	14.00	0.654
AB (Time, Stage)			
3 sec., D	2	19.90	1.307
3 sec., (EO)	2	14.55	1.307
60 sec., D	2	16.35	1.307
60 sec., (EO)	2	12.55	1.307
300 sec., D	2	26.20	1.307
300 sec., (EO)	2	15.10	1.307
1800 sec., D	2	28.70	1.307
1800 sec., (EO)	2	13.80	1.307

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEA $\log(CI/C_{100})$:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	0.230	7.650E-02	10.93**
B (Stage)	1	3.101	3.101	443.01**
AB	3	2.518E-02	8.396E-03	1.20
Error	8	5.600E-02	6.999E-03	
Total	15	3.412		

Term	Count	Mean	Standard Error
All	16	0.122	
A (Time)			
3 sec.	4	-4.99E-02	4.183E-02
60 sec.	4	7.965E-02	4.183E-02
300 sec.	4	0.188	4.183E-02
1800 sec.	4	0.269	4.183E-02
B (Stage)			
D	8	0.562	2.958E-02
(EO)	8	-0.318	2.958E-02
AB (Time, Stage)			
3 sec., D	2	0.374	5.916E-02
3 sec., (EO)	2	-0.474	5.916E-02
60 sec., D	2	0.471	5.916E-02
60 sec., (EO)	2	-0.312	5.916E-02
300 sec., D	2	0.634	5.916E-02
300 sec., (EO)	2	-0.257	5.916E-02
1800 sec., D	2	0.769	5.916E-02
1800 sec., (EO)	2	-0.231	5.916E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEP % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	2.2690E-02	8.968E-03	0.34
B (Stage)	1	2.095E-02	2.095E-02	0.79
AB	3	3.149E-02	1.049E-02	0.40
Error	8	0.211	2.641E-02	
Total	15	0.291		

Term	Count	Mean	Standard Error
All	16	0.800	
A (Time)			
3 sec.	4	0.810	8.125E-02
60 sec.	4	0.779	8.125E-02
300 sec.	4	0.860	8.125E-02
1800 sec.	4	0.750	8.125E-02
B (Stage)			
D	8	0.763	5.746E-02
(EO)	8	0.836	5.746E-02
AB (Time, Stage)			
3 sec., D	2	0.751	0.115
3 sec., (EO)	2	0.869	0.115
60 sec., D	2	0.794	0.115
60 sec., (EO)	2	0.764	0.115
300 sec., D	2	0.856	0.115
300 sec., (EO)	2	0.865	0.115
1800 sec., D	2	0.653	0.115
1800 sec., (EO)	2	0.847	0.115

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEP $\log(Cl/C_{100})$:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	0.154	5.121E-02	21.61**
B (Stage)	1	0.988	0.988	417.00**
AB	3	2.555E-02	8.518E-03	3.59*
Error	8	1.896E-02	2.370E-03	
Total	15	1.187		

Term	Count	Mean	Standard Error
All	16	0.231	
A (Time)			
3 sec.	4	7.872E-02	2.434E-02
60 sec.	4	0.221	2.434E-02
300 sec.	4	0.283	2.434E-02
1800 sec.	4	0.342	2.434E-02
B (Stage)			
D	8	0.480	1.721E-02
(EO)	8	-1.70E-02	1.721E-02
AB (Time, Stage)			
3 sec., D	2	0.387	3.443E-02
3 sec., (EO)	2	-0.229	3.443E-02
60 sec., D	2	0.481	3.443E-02
60 sec., (EO)	2	-3.86E-02	3.443E-02
300 sec., D	2	0.506	3.443E-02
300 sec., (EO)	2	6.055E-02	3.443E-02
1800 sec., D	2	0.545	3.443E-02
1800 sec., (EO)	2	0.139	3.443E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEN % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	2.962	0.987	0.94
B (Stage)	1	9.359	9.359	8.87**
AB	3	1.877	0.626	0.59
Error	8	8.444	1.055	
Total	15	22.642		

Term	Count	Mean	Standard Error
All	16	1.282	
A (Time)			
3 sec.	4	0.931	0.514
60 sec.	4	1.958	0.514
300 sec.	4	0.888	0.514
1800 sec.	4	1.352	0.514
B (Stage)			
D	8	2.047	0.363
(EO)	8	0.517	0.363
AB (Time, Stage)			
3 sec., D	2	1.482	0.726
3 sec., (EO)	2	0.380	0.726
60 sec., D	2	3.245	0.726
60 sec., (EO)	2	0.672	0.726
300 sec., D	2	1.271	0.726
300 sec., (EO)	2	0.505	0.726
1800 sec., D	2	2.190	0.726
1800 sec., (EO)	2	0.513	0.726

**Significant at 95% confidence level.

*Significant at 90% confidence level.

NVEEN log(C_l/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	0.444	0.148	3.04*
B (Stage)	1	1.588E-03	1.588E-03	0.03
AB	3	4.511E-03	1.503E-03	0.03
Error	8	0.390	4.871E-02	
Total	15	0.840		

Term	Count	Mean	Standard Error
All	16	3.802E-02	
A (Time)			
3 sec.	4	5.924E-02	0.110
60 sec.	4	-0.208	0.110
300 sec.	4	0.262	0.110
1800 sec.	4	3.823E-02	0.110
B (Stage)			
D	8	4.798E-02	7.803E-02
(EO)	8	2.804E-02	7.803E-02
AB (Time, Stage)			
3 sec., D	2	7.612E-02	0.156
3 sec., (EO)	2	4.236E-02	0.156
60 sec., D	2	-0.207	0.156
60 sec., (EO)	2	-0.208	0.156
300 sec., D	2	0.296	0.156
300 sec., (EO)	2	0.229	0.156
1800 sec., D	2	2.741E-02	0.156
1800 sec., (EO)	2	4.906E-02	0.156

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Volatile % of total TOC:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	12.440	4.147	0.44
B (Stage)	1	15.049	15.049	1.60
AB	3	18.147	6.049	0.64
Error	6	56.320	9.387	
Total	13	105.274		

Term	Count	Mean	Standard Error
All	14	3.814	
A (Time)			
3 sec.	4	5.145	1.532
60 sec.	3	3.140	1.769
300 sec.	4	2.467	1.532
1800 sec.	3	4.511	1.769
B (Stage)			
D	8	4.674	1.083
(EO)	6	2.668	1.251
AB (Time, Stage)			
3 sec., D	2	5.015	2.166
3 sec., (EO)	2	5.275	2.166
60 sec., D	2	3.151	2.166
60 sec., (EO)	1	3.120	3.064
300 sec., D	2	4.220	2.166
300 sec., (EO)	2	0.713	2.166
1800 sec., D	2	6.310	2.166
1800 sec., (EO)	1	0.913	3.064

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Volatile log(Cl/C_{100}):

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Time)	3	0.862	0.287	0.66
B (Stage)	1	0.173	0.173	0.40
AB	3	0.680	0.227	0.52
Error	8	1.298	0.433	
Total	15	3.627		

Term	Count	Mean	Standard Error
All	11	0.324	
A (Time)			
3 sec.	4	-0.140	0.329
60 sec.	3	0.658	0.380
300 sec.	2	0.576	0.465
1800 sec.	2	0.498	0.465
B (Stage)			
D	6	0.508	0.269
(EO)	5	0.102	0.294
AB (Time, Stage)			
3 sec., D	2	0.156	0.465
3 sec., (EO)	2	-0.437	0.465
60 sec., D	2	0.882	0.465
60 sec., (EO)	1	0.210	0.658
300 sec., D	1	0.260	0.658
300 sec., (EO)	1	0.893	0.658
1800 sec., D	1	0.712	0.658
1800 sec., (EO)	1	0.283	0.658

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Appendix 9F: TOC/ΔKappa Data

Comparison of OC(EO), OD(EO), and D(EO) Sequences:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	2	6.413E-02	3.206E-02	7.89*
Error	3	1.219E-02	4.066E-03	
Total	5	7.633E-02		

Term	Count	Mean	Standard Error
All	6	1.177	
A (Sequence)			
OC(EO)	2	1.320	4.509E-02
OD(EO)	2	1.080	4.509E-02
D(EO)	2	1.130	4.509E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Comparison of D Stage pH in the OD(EO) Sequence:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	1	7.224E-03	7.224E-03	7.81
Error	2	1.850E-03	9.250E-04	
Total	3	9.074E-03		

Term	Count	Mean	Standard Error
All	4	1.118	
A (pH)			
pH 2	2	1.075	2.150E-02
pH 4	2	1.160	2.150E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Comparison of D Stage Reaction Time in the OD(EO) Sequence:

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	3	5.065E-02	1.688E-02	3.73
Error	4	1.810E-02	4.525E-03	
Total	7	6.875E-02		

Term	Count	Mean	Standard Error
All	8	1.253	
A (Time)			
3 seconds	2	1.390	4.756E-02
60 seconds	2	1.200	4.756E-02
300 seconds	2	1.215	4.756E-02
1800 seconds	2	1.205	7.756E-02

**Significant at 95% confidence level.

*Significant at 90% confidence level.

Appendix 9G: Percentage of Low (< 1000) Molecular Weight Material in Bleaching Effluents

Source	DF	Sum of Squares	Mean Square	F-Ratio
A (Sequence)	7	149793.4	21399.05	132.35**
B (Stage)	1	153458	153458	949.10**
AB	7	24077.5	3439.64	21.27**
Error	16	2587	161.69	
Total	31	329915.9		

Term	Count	Mean	Standard Error
All	32	738.56	
A (Sequence)			
1: OC(EO)	4	894.25	6.36
2: OD(EO)	4	757.75	6.36
3: OD(EO)-pH 4	4	761.75	6.36
4: D(EO)	4	753.25	6.36
5: OD(EO)-30 min	4	705.75	6.36
6: OD(EO)-5 min	4	666.50	6.36
7: OD(EO)-1min	4	684.50	6.36
8: OD(EO)-3 sec	4	684.75	6.36
B (Stage)			
1: D or C Stage	16	807.81	3.18
2: (EO) Stage	16	669.31	3.18
A, B: (Seq., Stage)			
1, 1	2	935.00	8.99
1, 2	2	853.50	8.99
2, 1	2	812.00	8.99
2, 2	2	703.50	8.99
3, 1	2	779.00	8.99
3, 2	2	744.50	8.99
4, 1	2	834.50	8.99
4, 2	2	672.00	8.99
5, 1	2	800.00	8.99
5, 2	2	611.50	8.99
6, 1	2	749.50	8.99
6, 2	2	583.50	8.99
7, 1	2	763.50	8.99
7, 2	2	605.50	8.99
8, 1	2	789.00	8.99
8, 2	2	580.50	8.99

**Significant at 95% Confidence

*Significant at 90% Confidence

APPENDIX 10: TABLES OF SIGNIFICANT DIFFERENCES

Appendix 10A: Comparison of OC(EO), OD(EO), and D(EO) Bleaching Sequences

Comparisons: OC(EO) vs OD(EO): A
OD(EO) vs D(EO): B

Significance: Not Significant: N
Significant at 90% Confidence: 90
Significant at 95% Confidence: 95
*Only OD(EO) and D(EO) Data Used in Analysis

Fraction	Comparison	TOC (kg/t) D/C Stage	TOC (kg/t) (EO) Stage
Whole	A	95	95
	B	95	95
Fraction	**Comparison**	**% of Total TOC D/C Stage**	**% of Total TOC (EO) Stage**
NVEE I	A	95	95
	B	N	90
NVEE II	A	N	N
	B	90	N
NVNEE	A	N	N
	B	N	N
NVEEA	A	N	95
	B	90	90
NVEEP	A	95	90
	B	N	N
NVEEN	A	N	N
	B	N	N
Volatiles	A	N	N
	B	N	N
Fraction	**Comparison**	**Cl/C_{100} D/C Stage**	**Cl/C_{100} (EO) Stage**
Whole	A	95	95
	B	N	95
NVEE I	A	95	95
	B	N	N

Fraction	Comparison	Cl/C_{100} D/C Stage	(EO) Stage
NVEE II	A	N	95
	B	95	95
NVNEE	A	95	95
	B	95	95
NVEEA	A	95	95
	B	N	95
NVEEP	A	95	95
	B	N(95*)	N(95*)
NVEEN	A	95	95
	B	95	95
Volatiles	A	N	N
	B	N	N

Appendix 10B: Comparison of pH 2 and pH 4 D Stages in the OD(EO) Bleaching Sequence

Comparisons: pH 2 vs pH 4: A

Significance: Not Significant: N
Significant at 90% Confidence: 90
Significant at 95% Confidence: 95
*Calculated Data Not Used in Analysis

Fraction	Comparison	TOC (kg/t) D Stage	(EO) Stage
Whole	A	95	N
Fraction	**Comparison**	**% of Total TOC D Stage**	**(EO) Stage**
NVEE I	A	N(90*)	N(90*)
NVEE II	A	N	N
NVNEE	A	N	N
NVEEA	A	N	N
NVEEP	A	95	95
NVEEN	A	N	N
Volatiles	A	N	N
Fraction	**Comparison**	**Cl/C_{100} D Stage**	**(EO) Stage**
Whole	A	95	95
NVEE I	A	95	95
NVEE II	A	N	N
NVNEE	A	N	N
NVEEA	A	N	N
NVEEP	A	95	95
NVEEN	A	N	N
Volatiles	A	N	N

Appendix 10C: Comparison of D Stage Reaction Time in the OD(EO) Bleaching Sequence

Comparisons:
3 seconds vs 60 seconds: A
3 seconds vs 300 seconds: B
3 seconds vs 1800 seconds: C
60 seconds vs 300 seconds: D
60 seconds vs 1800 seconds: E
300 seconds vs 1800 seconds: F

Significance:
Not Significant: N
Significant at 90% Confidence: 90
Significant at 95% Confidence: 95

Fraction	Comparison	TOC (kg/t) D Stage	TOC (kg/t) (EO) Stage
Whole	A	95	N
	B	95	95
	C	95	N
	D	95	95
	E	95	N
	F	95	95

Fraction	Comparison	% of Total TOC D Stage	% of Total TOC (EO) Stage
NVEE I	A	N	N
	B	N	N
	C	95	95
	D	N	N
	E	90	90
	F	N	N
NVEE II	A	N	N
	B	N	N
	C	N	N
	D	N	N
	E	N	N
	F	N	N
NVNEE	A	N	N
	B	N	N
	C	N	N
	D	N	N
	E	N	N
	F	N	N

Fraction	Comparison	% of Total TOC	
		D Stage	(EO) Stage
NVEEA	A	N	N
	B	N	N
	C	95	95
	D	N	N
	E	95	95
	F	90	90
NVEEP	A	N	N
	B	N	N
	C	N	N
	D	N	N
	E	N	N
	F	N	N
NVEEN	A	N	N
	B	N	N
	C	N	N
	D	N	N
	E	N	N
	F	N	N
Volatiles	A	N	N
	B	N	N
	C	N	N
	D	N	N
	E	N	N
	F	N	N

Fraction	Comparison	% Of Total AOX	
		D Stage	(EO) Stage
NVEE I	A	95	95
	B	N	N
	C	N	N
	D	95	95
	E	95	95
	F	N	N
NVEEA	A	N	N
	B	95	N
	C	95	N
	D	95	N
	E	95	N
	F	N	N

Fraction	Comparison	Cl/C_{100} D Stage	Cl/C_{100} (EO) Stage
Whole	A	95	95
	B	95	95
	C	95	95
	D	95	95
	E	95	95
	F	95	95
NVEE I	A	N	N
	B	95	95
	C	95	95
	D	95	95
	E	95	95
	F	N	N
NVEE II	A	90	90
	B	95	95
	C	95	95
	D	N	N
	E	N	N
	F	N	N
NVNEE	A	95	95
	B	95	95
	C	95	95
	D	N	N
	E	95	95
	F	95	95
NVEEA	A	90	90
	B	95	95
	C	95	95
	D	N	N
	E	95	95
	F	N	N
NVEEP	A	95	95
	B	95	95
	C	95	95
	D	N	N
	E	95	95
	F	N	N

Fraction	Comparison	Cl/C_{100} D/C Stage	Cl/C_{100} (EO) Stage
NVEEN	A	N	N
	B	N	N
	C	N	N
	D	95	95
	E	N	N
	F	N	N
Volatiles	A	N	N
	B	N	N
	C	N	N
	D	N	N
	E	N	N
	F	N	N

APPENDIX 11: LOTUS SPREADSHEET FOR GPC DATA TRANSFORMATION

Appendix 11A contains a printout of the Lotus 123 spreadsheet that was used to transform raw GPC data into chromatograms and cumulative molecular weight distributions. The spreadsheet was written by Clark Woitkovich, a scientist in the Pulping and Bleaching group at the Institute of Paper Science and Technology. Appendix 11B provides instructions for using the spreadsheet.

Appendix 11A: Lotus Spreadsheet

	A	B	C	D
1		\A	{GOTO}N10~	
2	***	----->	+((E10*FR)-HMWS)/(LMWS-HMWS)~	
3			/C~N11..N150~	*FR=FLOW RATE (ML/MIN)
4			{GOTO}D10~	*HMWS=RET. VOL. OF HIGH
5	***	----->	@AVG(F__..F__)~	MOLECULAR WEIGHT STANDARD
6			/RV~~	(ML)
7			/C~D11..D150~	*LMWS=RET. VOL. OF LOW
8			{GOTO}H10~	MOLECULAR WEIGHT STANDARD
9			+F10-D10~	(ML)
10			/C~H11..H150~	
11			/RVH10..H150~~	
12			/RED10..D150~	
13			{GOTO}G1~	
14	***	----->	/GXG10..G__~AF10..F__~BH10..H__~	
15			CI10..I__~DK10..K__~EO10..O__~V~	
16				
17		\B	{GOTO}K10~	
18			+H10-I10~	
19			/C~K11..K150~	
20			{GOTO}L1~	
21			/GA{ESC}~OSYMQQV~	
22				
23				
24		\C	{GOTO}L10~	
25	***	----->	+E10*FR~	*FR=FLOW RATE (ML/MIN)
26			/C~L11.L150~	
27			{GOTO}M11~	
28			+(L11-L10)*(@AVG(K10..K11))~	
29			/C~M12.M150~	
30			{GOTO}M5~	
31	***	----->	@SUM(M10..M__)~	
32			{GOTO}D10~	
33			{LET D10,1000/M5}	
34			/C~D11.D150~	
35			{GOTO}O10~	
36			+K10*D10~	
37			/C~O11.O150~	
38			/RVO10..O150~~	
39			/RVL10..L150~P10..P150~	
40			/RED10..D150~	
41			{GOTO}L1~	
42	***	----->	/GXN10..N__~AF10..F__~B{ESC}	
43			~C{ESC}~D{ESC}~OSYAQQV~	
44				
45				
46				
47				
48				
49				
50				

	E	F
1		
2		
3		
4		
5		
6		
7		
8	min	TOC
9		
10		
11		
12		
13		
14		
15		
16		
17		
18		
19		
20		
21		
22		
23		
24		
25		
26		
27		
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37		
38		
39		
40		
41		
42		
43		
44		
45		
46		
47		
48		
49		
50		

	G	H	I	J
1			left	right
2	***	-------> x	(F5) +N__	(F5) +N__
3	***	-------> y	(F5) +H__	(F5) +H__
4				
5		slope	(F5) (J3-I3)/(J2-I2)	
6		int	(F5) +J3-(I5*J2)	
7			+(N__*SLOPE)+INTERCEPT	
8	cell	left0 TOC	ramp	
9			*** ----->	
10	10			
11	11			
12	12			
13	13			
14	14			
15	15			
16	16			
17	17			
18	18			
19	19			
20	20			
21	21			
22	22			
23	23			
24	24			
25	25			
26	26			
27	27			
28	28			
29	29			
30	30			
31	31			
32	32			
33	33			
34	34			
35	35			
36	36			
37	37			
38	38			
39	39			
40	40			
41	41			
42	42			
43	43			
44	44			
45	45			
46	46			
47	47			
48	48			
49	49			
50	50			

	K	L	M
1			
2			
3			
4			
5		!!! ---->	0
6			
7			integ TOC
8	flat TOC	ml	(micro gm)
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			
31			
32			
33			
34			
35			
36			
37			
38			
39			
40			
41			
42			
43			
44			
45			
46			
47			
48			
49			
50			

	N	O	P
1			
2		TO SAVE	
3		FOR OVERLAY PLOTS	
4		----------	
5		INTEPOLATION FORMULA	
6		(((N8-N7)/(N9-N7))*(O9-O7))+O7	
7			
8		RRV norm TOC	ml
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			
31			
32			
33			
34			
35			
36			
37			
38			
39			
40			
41			
42			
43			
44			
45			
46			
47			
48			
49			
50			

	Q	R
1		
2		
3		
4		
5		
6	0	0
7	integ norm TOC	integ
8	(micro gm)	intervals
9		
10		
11		
12		
13		
14		
15		
16		
17		
18		
19		
20		
21		
22		
23		
24		
25		
26		
27		
28		
29		
30		
31		
32		
33		
34		
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37		
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Appendix 11B: Instructions

Most of the spreadsheet operations are done using 3 macros. These macros are shown in columns A-D, and are run by typing the code of the macro (A, B, or C) while depressing the ALT key. Because operations are done by the macros, few formulas are present in the spreadsheet until the macros are run. At that time the formulas are placed in the sheet.

Non-transformed GPC data, consisting of cumulative time (minutes) and TOC (ppm) data pairs, are entered in columns E and F, beginning at row 10. The data should be entered into a separate spreadsheet, and the data sheet combined with this transformation spreadsheet such that the time and TOC data appear in the proper locations. Data may be entered in rows 10-150, resulting in a maximum of 140 entered data pairs. The user should note the row number of the final data point.

Additional data must be entered into the macros in columns A-D before each new set of data is analyzed. This printout contains blanks or variable names where data must be entered. The actual spreadsheet will contain numbers there. Changes are made throughout the spreadsheet by editing the formulas. The location of each spreadsheet macro cell that requires a data input is marked by 3 stars and an arrow in column A.

Cell B2 contains the relative retention volume formula, into which the eluent flow rate (ml/min) and the retention volumes of both the highest molecular weight standard and lowest molecular weight standards (ml) are entered.

Cell B5 contains a formula which requires the input of a range of rows from column F corresponding to a representative portion of the chromatogram baseline prior to sample elution (left baseline). Column F data should be inspected to determine the appropriate range for a baseline, and these row numbers are entered into the formula in cell

B5. The entire left baseline can be used from cell F10 up to the last cell before the excluded peak begins (commonly F36 or greater). A smaller representative portion of this entire range may also be used. This formula calculates an average baseline value that is subtracted from all data. This zeros the left baseline.

The number of rows of entered GPC data must be input in several locations. Data extends from row 10 to an undefined row, dependent on the length of the data set. The blanks in the formulas in cells B14-B15, B31, and B42-B43 should all be filled with the row number of the last data point (for example, row 100). The formula in cell B25 requires that the eluent flow rate (ml/min) be input.

Macro A is now run. The program will display on the screen the initial chromatogram and the chromatogram with the left baseline zeroed. Both will be on a relative retention volume basis on the x-axis. The ESC key is pressed 4 times to move on. The spreadsheet returns to the screen at column H.

Now the left baseline has been zeroed, but the right baseline is still most likely higher or lower than zero. Macro B is used to zero the right baseline. It subtracts a linear ramp from the chromatogram. The program must first have the initial and final points of this linear ramp entered. Column H (labeled left 0 TOC) is inspected to determine at which row the left baseline ends (one row prior to the beginning of the excluded peak) and at which row the right non-zeroed baseline begins. The row number at which the left baseline ends is entered into the blanks in the formulas in cells I2 and I3. The row number at which the final baseline begins is entered into the blanks in the formulas in cells J2 and J3. The x and y values of the endpoints of the ramp are displayed in these cells, and the slope and intercept of the line are displayed in cells I5 and I6. The formulas used for these calculations are displayed in the column I and J cells of this printout, but in the actual spreadsheet the calculated values appear in the cells.

Now that the slope and intercept of the linear ramp connecting the 2 baseline points are known, the equation of the line is written in the format shown in cell I7. The formula is written in cell J8. The blank in the formula should be replaced by the final row number of the left baseline (the same row number as entered into cells I2 and I3). The formula is then moved to the final row number of the left baseline in column I (the same as that entered in cells I2 and I3). The formula is copied to all row I cells until the first row number of the final baseline (the same row number entered in cells J2 and J3).

Macro B is now run. Macro B subtracts the linear ramp in column I from the data in column H, giving a chromatogram with both the left and right baselines zeroed. The chromatograms both before and after zeroing the right baseline are displayed on the screen using an expanded y-axis scale. The ESC key is pressed 4 times to move on. The spreadsheet returns to the screen under column K.

Macro C integrates the chromatogram and normalizes its area to 1000 μg TOC. The integration formula is given in cell B28. This formula determines the area for each time interval of the chromatogram, and the area of each interval is displayed in column M after the macro is run. To determine total integrated area, these area intervals are summed. The summation formula is given in cell M5 and must be edited for the proper column length (to sum only the column M rows with data, and to include all column M rows with data).

Macro C is now run, and displays on the screen both the final normalized chromatogram and the initial chromatogram. The ESC key is pressed 4 times to move on. The spreadsheet returns under column O. Columns N and O display the data from the normalized chromatogram on a relative retention volume x-axis scale. These data are extracted to a different file for subsequent chromatogram graphing.

The final operation is the determination of chromatogram area between the elution points of each standard. This information is needed to produce cumulative molecular weight distributions.

The relative retention volumes (RRV) for all standards must be known. The value for the highest molecular weight standard is 0.0 and that for the lowest molecular weight standard is 1.0. All other standards have values between. Since it is unlikely that the standard relative retention volumes will correspond to values taken during effluent analysis, the standard RRV values are inserted in the appropriate location in column N. For example, a standard RRV of 0.08 would be inserted between 0.05 and 0.1. This inserted RRV value has no chromatogram TOC value (column O) or retention volume value (column P) associated with it. So blank spaces are inserted in columns O and P and the interpolated chromatogram TOC and retention volume values are entered using the interpolation formula given in cell O6. The formula is copied to all empty column O and P cells which correspond to a standard RRV that was inserted. The RRV for all standards are similarly inserted and the interpolations for normalized TOC and retention volume made in each case. If by chance a standard RRV value is identical to an effluent value, no insertion or interpolation are necessary.

Next, the integrated normalized chromatogram TOC, including interpolated points, is integrated. This is done in column Q. The integration formula is copied from cell M10 to all cells in column Q that correspond to rows containing data (from row 10 to the last row containing data). There will be more rows of data here that in previous rows because of the insertion of additional RRV values and corresponding interpolated TOC readings. The sum of the integrated normalized TOC intervals is given in cell Q6. This summation formula is edited for the proper length column. If everything is correct, this will indicate 1000 μg TOC in cell Q6. If not, the column length of the summation formula is incorrect.

Cell R6 contains the summation formula for column R. This formula is adjusted for the same length as the formula in cell Q6. The first integration interval determines the area of the chromatogram corresponding to the material with a molecular weight higher than the highest molecular weight standard. In this case the summation formula from R6 is copied to the row in column R in which the highest molecular weight standard RRV (0.0) exists. The formula is edited so that it sums areas from cell Q10 to the row in column Q corresponding to the highest molecular weight standard RRV value.

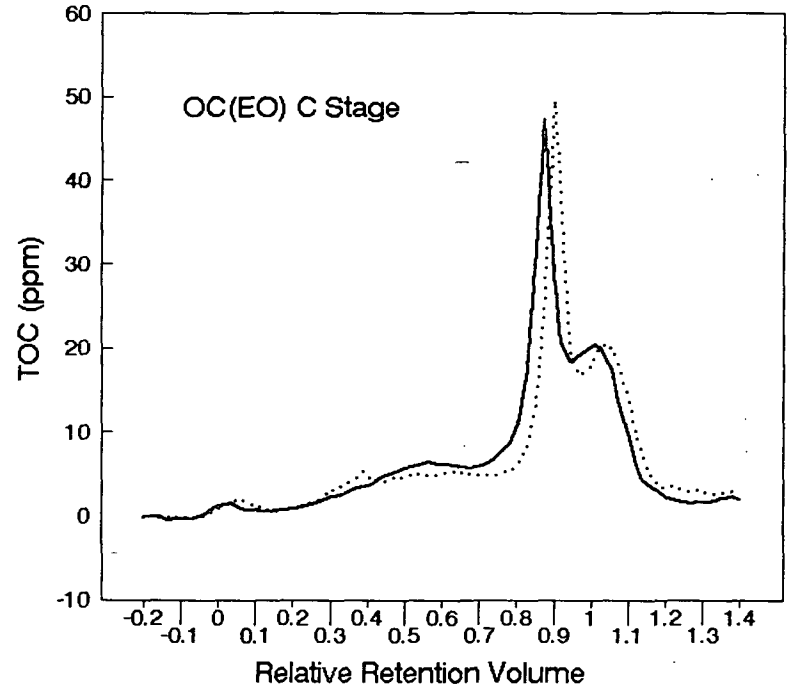
Areas between standards (standards A and B) are determined similarly. The summation formula is copied to the row in column R which corresponds to the standard B RRV value. The formula is edited so that it sums the areas from the row in column Q corresponding to 1 cell immediately after standard A to the row in column Q corresponding to standard B. This formula calculates the area between the elution of standards A and B. All other intervals between standards are similarly calculated.

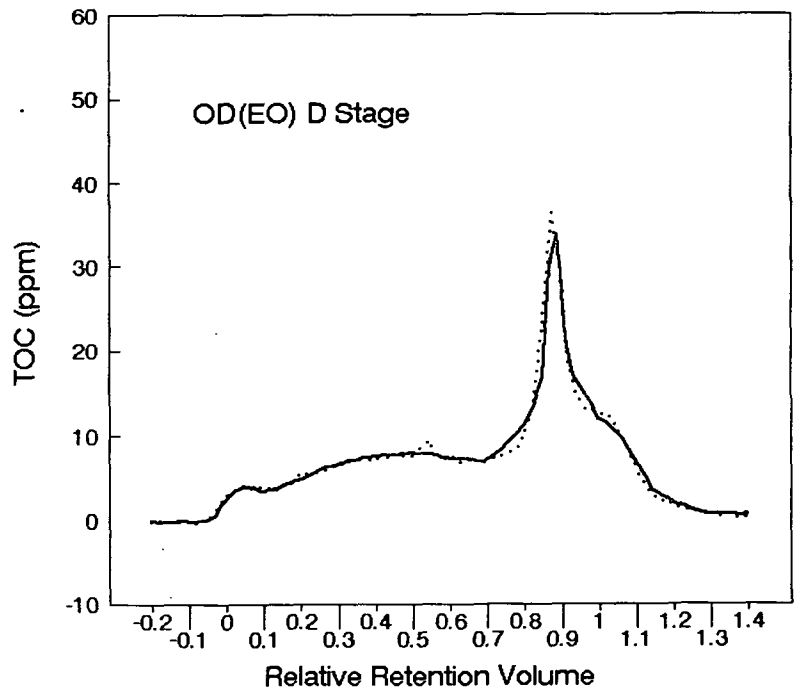
Finally, the area of the chromatogram corresponding to material with a lower molecular weight than the lowest molecular weight standard is determined. The summation formula is copied to the row in column R which corresponds to the last RRV value. The formula is edited so that it sums the areas from the column Q row corresponding to 1 cell after the lowest molecular weight standard (one cell after that corresponding to a RRV of 1.0) to the column Q row corresponding to the last RRV value.

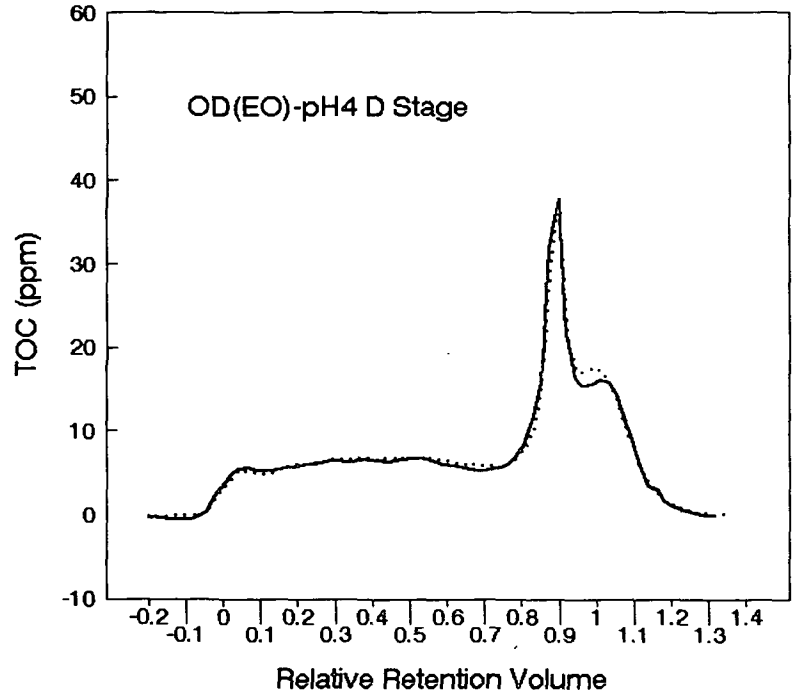
If all was correctly done, the summed area (in μg) in column R6 will be 1000. If this is not so, either the entire range was not done (if R6 is less than 1000), or overlap of integration intervals occurred (if R6 is greater than 1000).

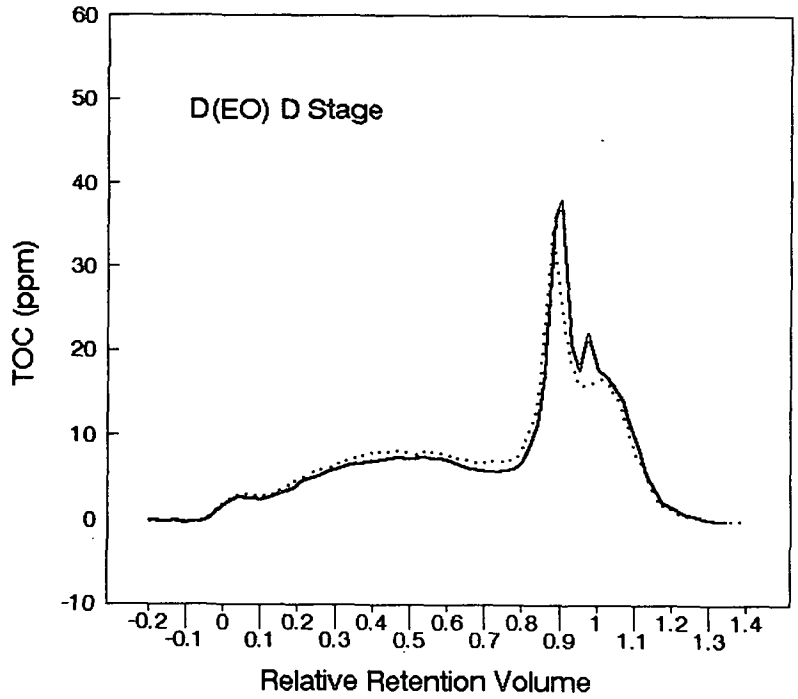
APPENDIX 12: REPLICATE GEL PERMEATION CHROMATOGRAMS

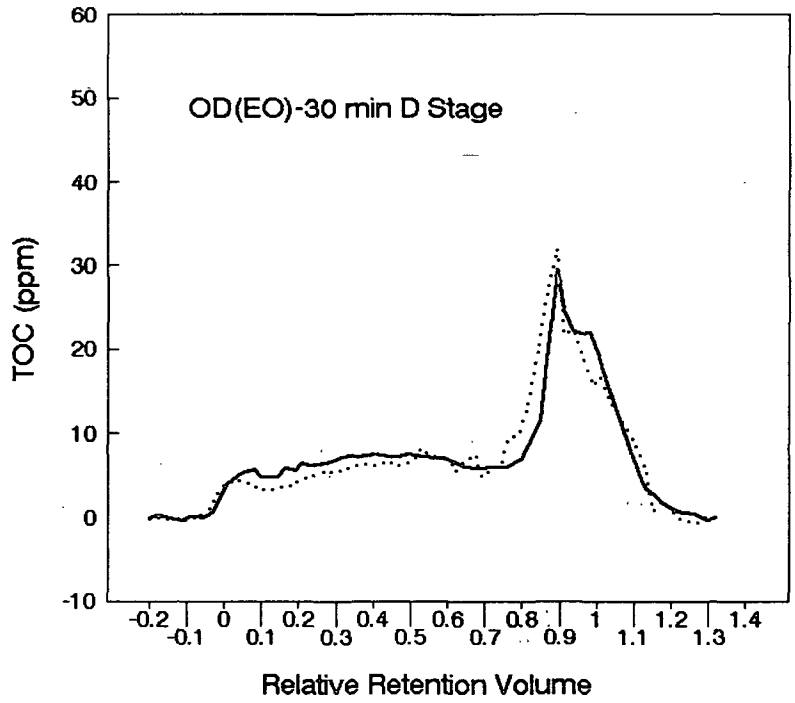
Appendix 12A: D or C Stage Effluents

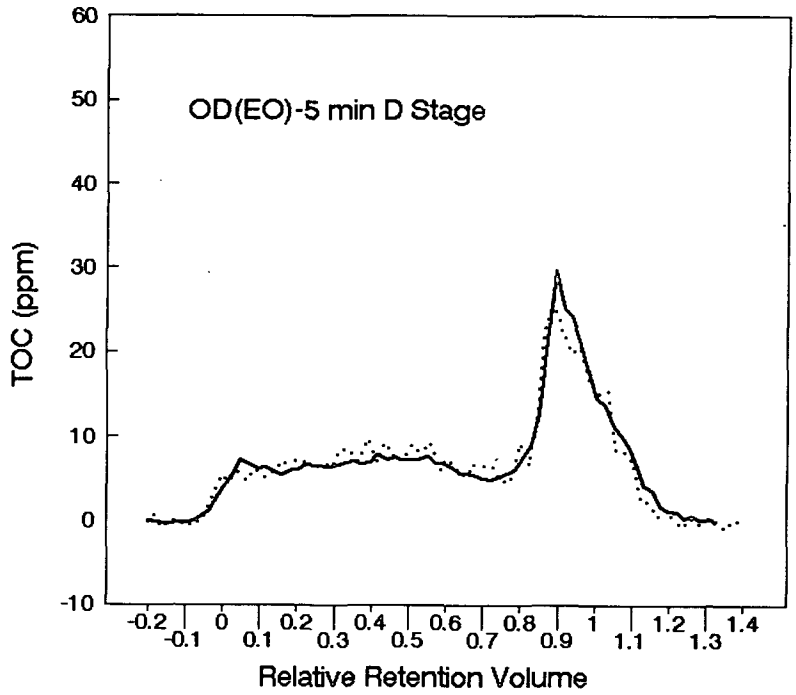


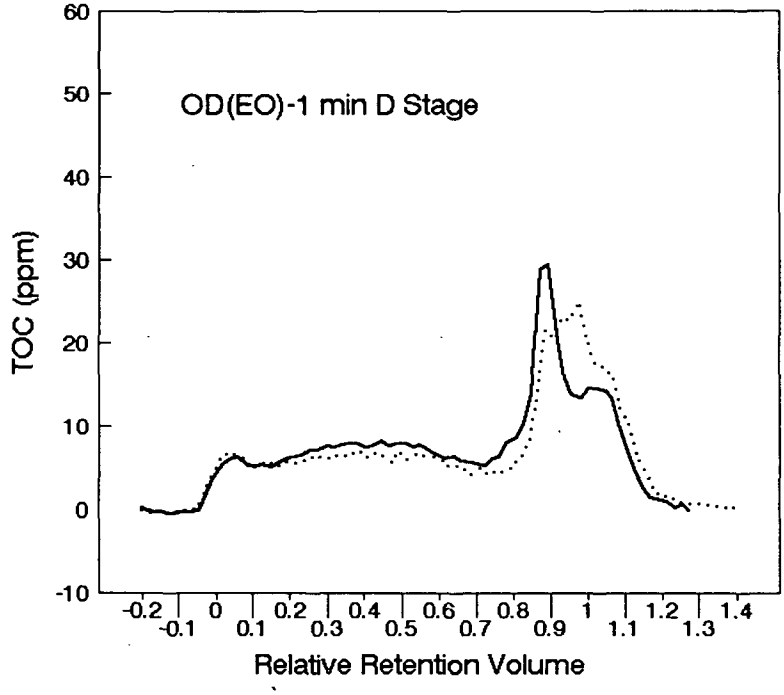


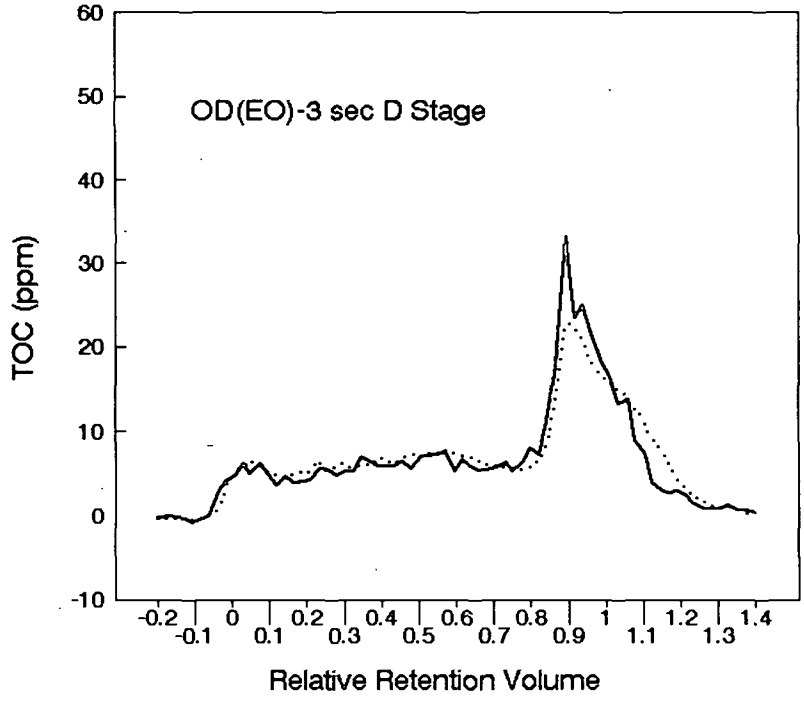

OD(EO)-pH4 D Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume


D(EO) D Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume

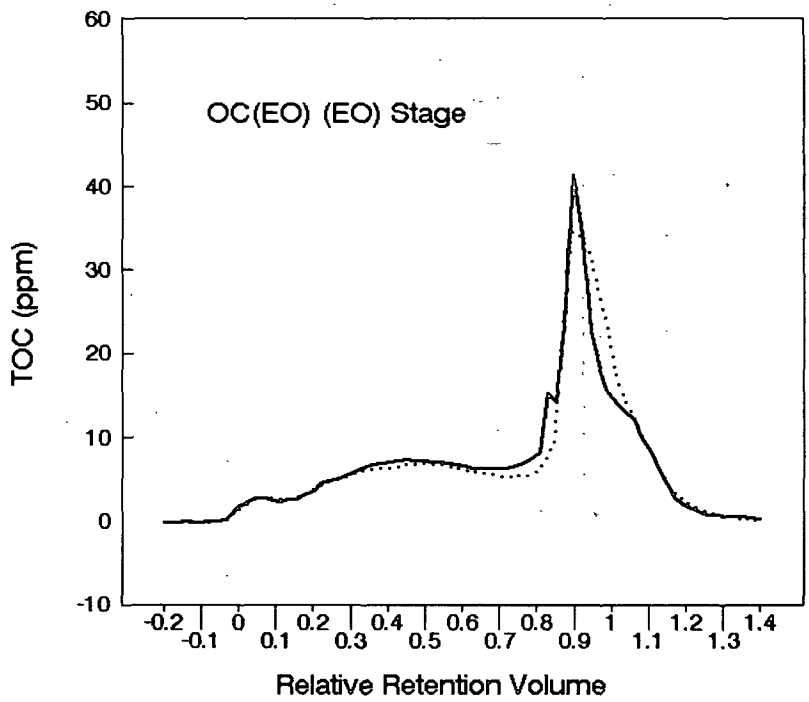

OD(EO)-30 min D Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume

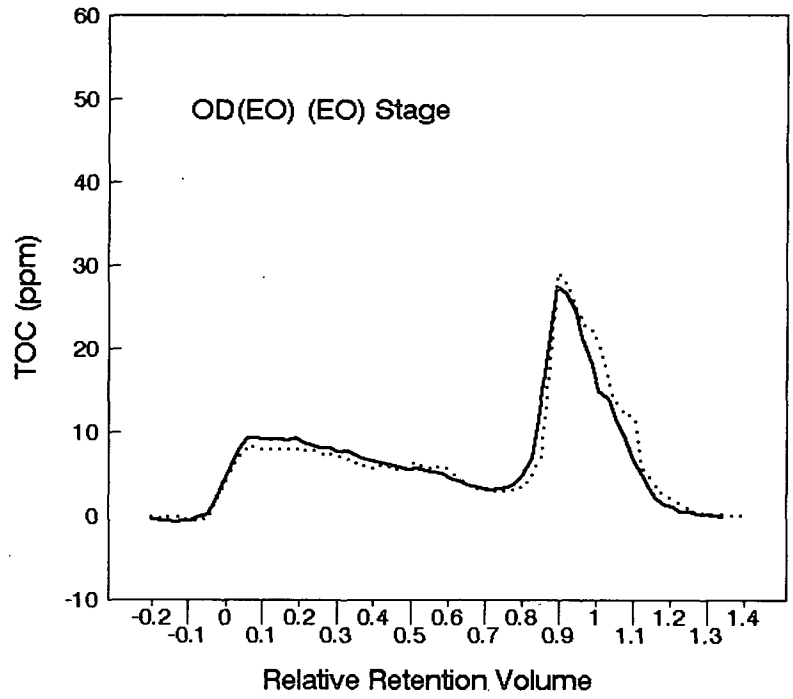

OD(EO)-5 min D Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume

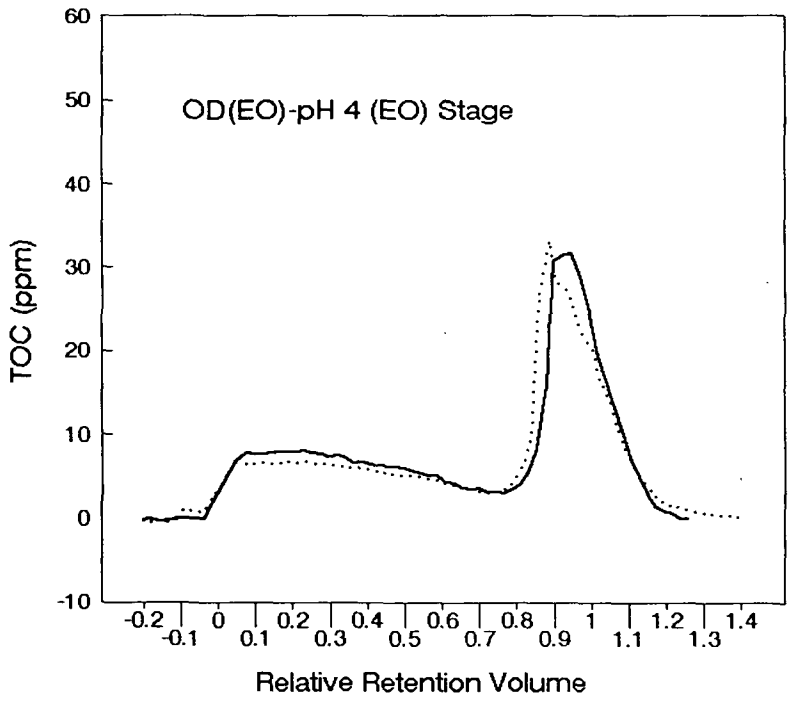

OD(EO)-1 min D Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume

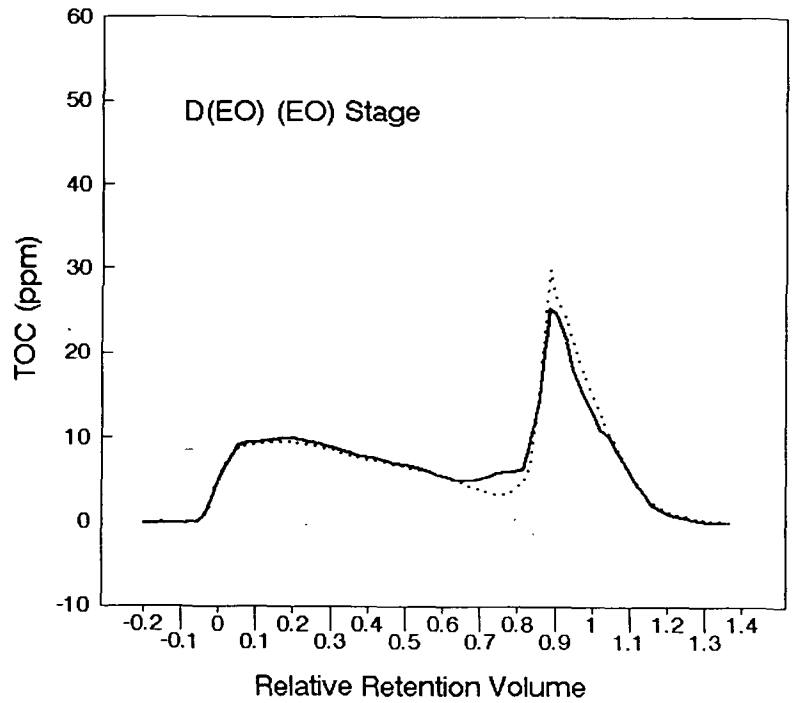

OD(EO)-3 sec D Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume

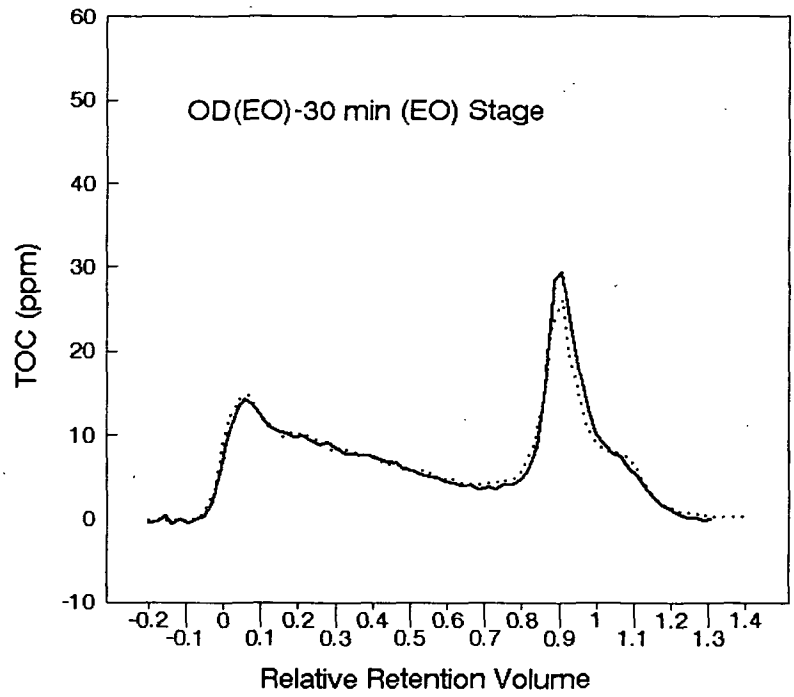
Appendix 12B: (EO) Stage Effluents

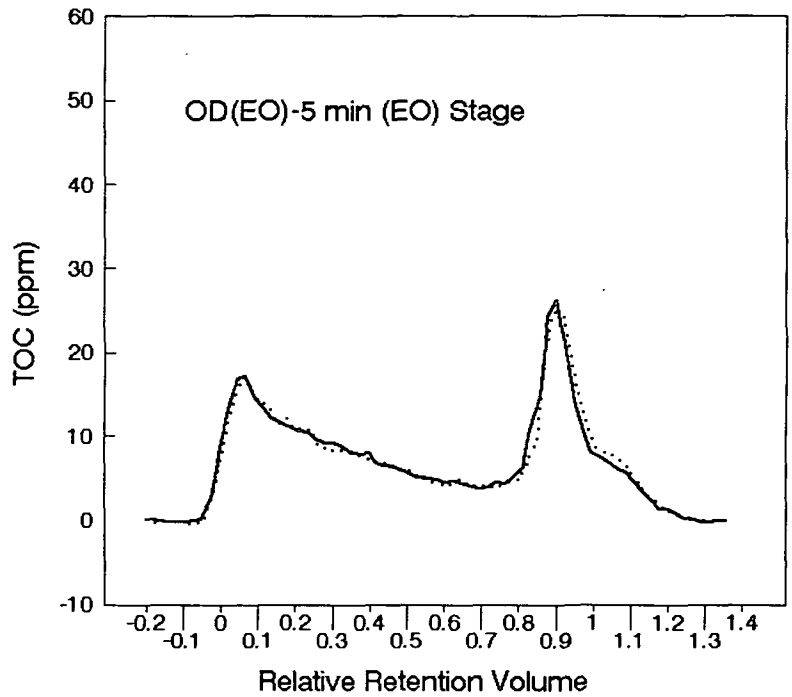


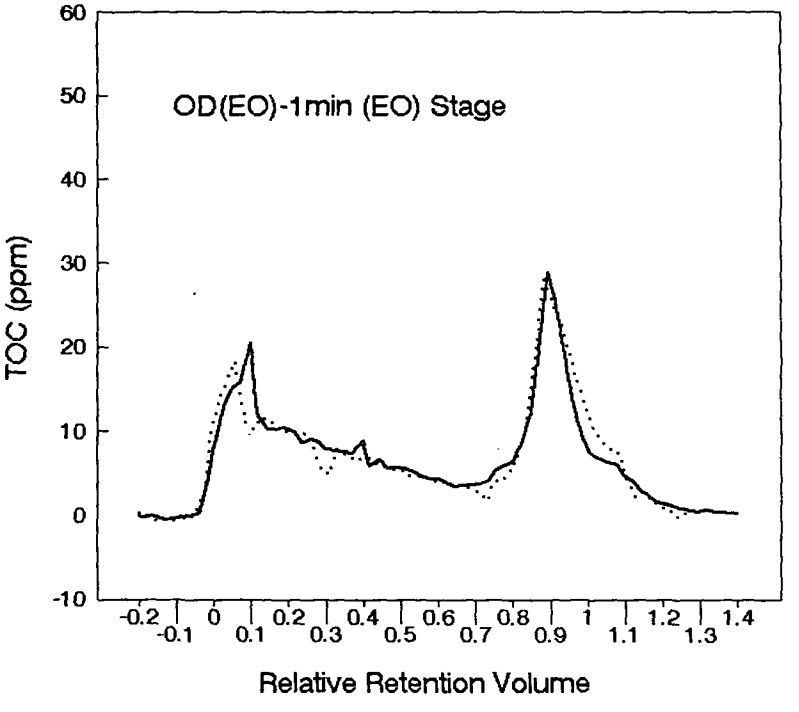


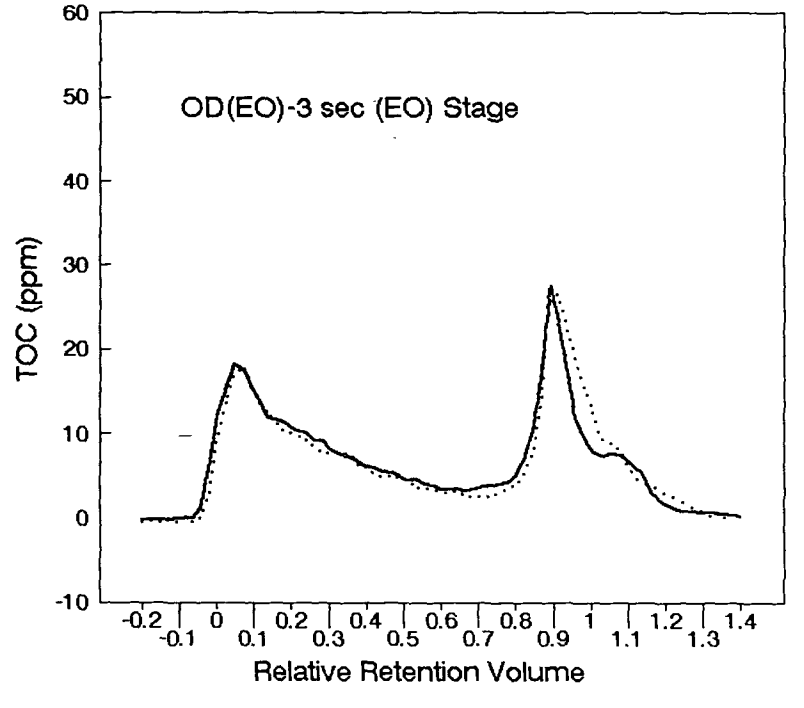

OD(EO)-pH 4 (EO) Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume


D(EO) (EO) Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume


OD(EO)-30 min (EO) Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume


OD(EO)-5 min (EO) Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume


OD(EO)-1min (EO) Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume


OD(EO)-3 sec (EO) Stage
TOC (ppm)
60
50
40
30
20
10
0
-10
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
1.4
Relative Retention Volume